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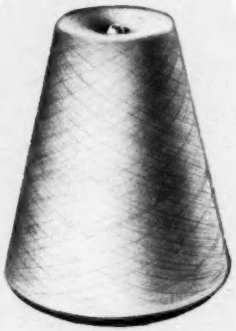

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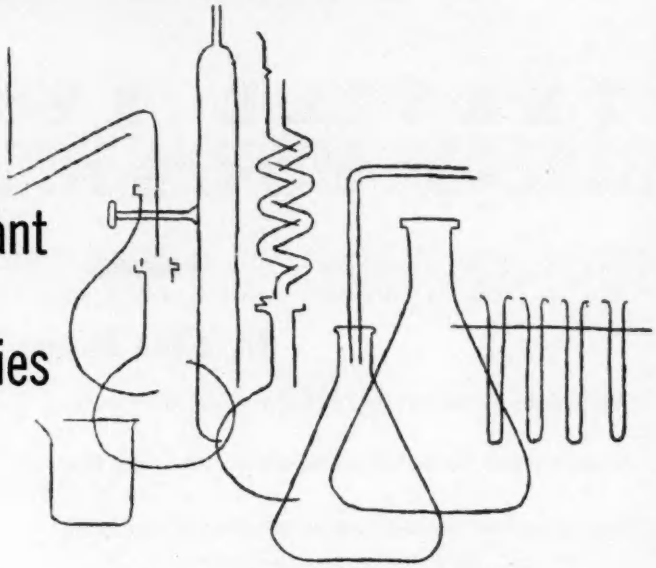

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TEXTILE RESEARCH JOURNAL

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The Copper Technique for Dyeing Acrylonitrile Fibers*

T. A. Feild, Jr., and G. H. Fremon

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Abstract

The use of small amounts of dissolved copper in the dye bath to improve the dyeing of acrylonitrile fibers is described. Cuprous copper, obtained by reducing cupric acetate or sulfate in the dye bath, is the preferred form. The technique appears to be specific to acrylonitrile fibers, and is most effective with acid, direct, and soluble acetate dyes. Data on sorption of copper and of other metal ions by acrylonitrile fibers and various non-acrylonitrile fibers are presented, and possible complexes between copper ions and polymeric acrylonitrile are postulated.

AS IN THE CASE of acetate rayon, the problem of dyeing has claimed a considerable amount of attention during the course of development of acrylonitrile fibers, of which dynel [2, 3], Vinyon N [1, 14], Orlon [11, 13], and Chemstrand [4] are prominent examples. Although on the basis of early experience the problem appeared quite formidable, it has actually turned out to be much less difficult than it was in the case of cellulose acetate, for example. It is possible to obtain acceptable results with dyes designed for wool, for cotton, and for cellulose acetate, and it has not been necessary to create new dyes specifically for the acrylonitrile fibers. These fibers behave differently from the more familiar natural fibers and rayons, however, and it has been necessary in some cases to develop special techniques in order to obtain results that are commercially satisfactory. The present paper is devoted primarily to one of these special techniques, which involves the use of dissolved copper as a dye assistant for acrylonitrile fibers.

General

In general, acrylonitrile fibers have greater "natural affinity" for the dispersed acetate dyes than for water-soluble dyes, and it is possible in some cases to obtain acceptable pastel shades by following the

*Based on report presented at the Annual Meeting of Textile Research Institute, New York City, Nov. 16, 1950.

technique ordinarily employed for dyeing cellulose acetate with these colors. The acrylonitrile fibers as a group have better stain-resistance than cellulose acetate, however, and they are swollen only very slightly by water, even at elevated temperatures. In order to obtain an equivalent degree of staining in a practical dyeing operation, therefore, it is necessary to use higher dye-bath temperatures than are customary in the case of cellulose acetate—hence the use of temperatures in the neighborhood of 210°F for dyeing dynel [6], for example, and above 212°F for dyeing polyacrylonitrile fibers [15]. In cases where higher temperatures alone do not yield deep enough shades, it is possible to loosen the molecular structure of the fiber further by using certain selected solvents or swelling agents that are not powerful enough to attack the crystalline regions of the fiber to any great extent, but are active enough to intrude into the amorphous regions. Many potential swelling agents have been studied during the course of development of dynel and Vinyon N fibers, and *p*-phenylphenol has been adopted as the most suitable for commercial use. Thus, in order to obtain very deep shades on dynel without using excessive amounts of dye, *p*-phenylphenol is included in the dye bath in amounts of the order of 2% on fabric.

The absorption of many acid and direct dyes by acrylonitrile fibers can also be enhanced by using swelling agents. In the case of these water-soluble dyes, however, absorption by the hydrophobic fibers is so low that it is difficult—often impossible—to obtain deep shades by employing this device. It was in connection with efforts to improve these results that the surprising effectiveness of dissolved copper as an aid to dyeing was discovered. The order of magnitude of this "copper effect" is illustrated in Figure 1, which shows dynel fabric dyed with and without the aid of copper using two different dyes: Pontamine Red 8BL (direct) and Xylene Milling Blue BL (acid). The numbers shown under the samples represent percent blue-light reflectance in the case of the red dye, and percent red-light reflectance in the case of the blue dye.

Further study of the phenomenon revealed that copper enhances the pickup of a wide variety of dyes, whether it is present in the dye bath in the metallic form or as dissolved cupric or cuprous salts. Of the three, dissolved cuprous salts, prepared by interaction in the dye bath between cupric sulfate or acetate and any one of a wide variety of reducing agents—dextrose, for example—appears to be the most effective. It was also found that copper is a dye assistant in its own right, not merely a promoter for dye assistants that act by swelling the fiber, and that this "copper technique" is specific to acrylonitrile fibers and is most effective with acid, direct, and soluble acetate dyes. Moreover, it was established that copper is beneficial only if the fabric is exposed to the copper solution before or during dyeing. In experiments thus far, aftertreatments with copper solutions appear to have no effect on color, depth of shade, fastness, light-stability or any other important property of dyed fabrics.

The experiments reported herein represent an exploratory effort to determine the magnitude of the copper effect, and to arrive at some plausible explanation of the mechanism involved. The general plan of this study may be summarized as follows: (1) effect of dissolved copper on absorption of dyes by various fibers and of various dyes by acrylonitrile copolymer fibers; (2) sorption of copper by various fibers; and (3) sorption of other metals by dynel, and trial of the more promising metals as dye assistants.

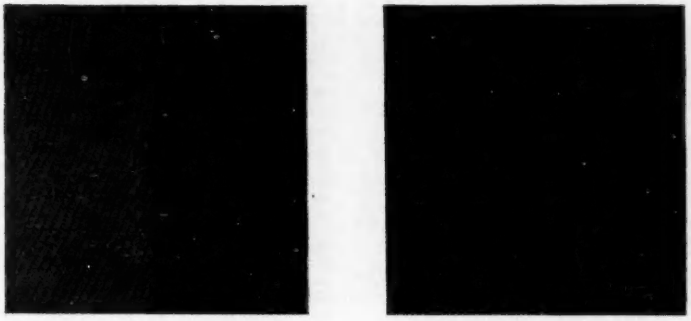
Experimental Procedure

Except where noted otherwise, the following procedure was followed in carrying out the dyeing experiments:

Swatches of knitted fabric were scoured at 160°F in a solution of nonionic detergent and rinsed thoroughly. The detergent used was Tergitol NPG, and the quantity 1.5%. (All concentrations are expressed as percentages of weight of fabric.)

A dye-bath ratio of 30:1 was employed. The dye bath was made up cold, and contained 2% of Peregal OK as leveling agent and 5% of dye. The pH of the dye bath was adjusted to 4.0 by addition of glacial acetic acid. *p*-Phenylphenol, when used, was added in concentration of 2.25%; it was first dissolved along with one-third its weight of solid sodium hydroxide in a small amount of boiling water, and then added to the dye bath. Copper, when used, was normally introduced in the form of cupric acetate—1% of $Cu(C_2H_3O_2)_2 \cdot H_2O$, or 0.32% of Cu^{++}—and was reduced to the cuprous state by addition of 0.4% of zinc formaldehydesulfoxylate (Sulfoxite S Conc.) to the dye bath.

The fabric was put into the dye bath at room temperature, and the temperature was then raised to a



19.5% BLR 11.8% BLR 16.5% RLR 10.5% RLR

FIG. 1. Left—*Samples of dynel fabric dyed with Pontamine Red 8BL dye. Reduced copper was used as promoter in the dyeing of the sample on the right.* Right—*Samples of dynel fabric dyed with Xylene Milling Blue BL dye. Reduced copper was used as promoter in the dyeing of the sample on the right.*

boil and held there for 90 min. After dyeing, the sample was rinsed, scoured at 170°F with 2% soap, and rinsed thoroughly. It was then dried for 20 min. at 250°F.

Direct measurements of depth of color were made by the light-reflectance method, using a Fisher Electrophotometer fitted with a filter of color approximately complementary to the color of dye employed. Quantity of dye absorbed was determined by dissolving the dyed fabric, usually in dimethyl formamide, and determining the effect on light-transmission of the solvent. (Calibration curves were prepared using each dye employed in this work.) Metal-ion content was determined by means of an emission spectrograph, quantitatively in the case of copper and tin, semi-quantitatively in the case of the other metals studied.

Specificity of the Copper Effect

To determine whether the apparent specificity of the copper effect to acrylonitrile copolymer fibers and to acid, direct, and soluble acetate dyes was real or only apparent, dyeing experiments were run on a variety of acrylonitrile and non-acrylonitrile fibers using several different dyes. The results of these experiments are summarized in Table I. *p*-Phenylphenol was used in all of the experiments with acid and direct dyes. In the case of the dispersed acetate dye, acid and *p*-phenylphenol were omitted and 1.5% of Tergitol 7 wetting agent was added to the formula. The procedure employed for applying vat dye necessarily differed from that outlined in the previous section. The bath was made alkaline with 1.8% of sodium hydroxide (on fabric), and 0.9% of sodium hydrosulfite was added to reduce the dye to the leuco form. The bath was heated to 60°C for 45 min., after which 1% of sodium perborate was added to oxidize the dye and the bath temperature was held at 60°C for an additional 30 min.

It was not possible to dissolve all of the dyed samples for quantitative measurement of dye content, and, in addition, the supplies of Orlon staple and of Chemstrand at hand were severely limited. Color is therefore expressed in Table I in terms of light reflectance in all cases, and in terms of actual dye content where possible. The correlation between the two methods of indicating color is fairly good.

Effectiveness of Various Forms of Copper

The experiments summarized in Table II were all run on dynel fabric, using Croceine Scarlet MOO (acid) dye and the usual 2.25% of *p*-phenylphenol.

Effectiveness of Copper as Sole Dye Assistant

Two additional experiments were run under conditions identical with those described above, omitting both copper and *p*-phenylphenol in one case and using reduced copper alone in the other. The results, including the "control" value of Table II, are shown in Table III, from which it is apparent that reduced copper alone is a more effective dye assistant than *p*-phenylphenol.

TABLE I. SPECIFICITY OF COPPER EFFECT

Fiber	Dye	Dye type	Light reflectance (%)			Dye pickup (% on wt. of fiber)		Ratio
			Undyed sample	Dyed: Without copper	Dyed: With copper	No copper	Using copper	copper / no copper
Wool	Croceine Scarlet MOO	Acid	50.0	8.8	10.0*	Sample not soluble		
Cotton	Croceine Scarlet MOO	Acid	74.5	22.5	20.5	Sample not soluble		
Viscose rayon	Croceine Scarlet MOO	Acid	80	40	32.0	Sample not soluble		
Acetate rayon	Croceine Scarlet MOO	Acid	79	24	21.0	0.092	0.155	1.7
Nylon	Croceine Scarlet MOO	Acid	80	7	6.5	Sample not soluble		
Dacron	Croceine Scarlet MOO	Acid	65.5	29.5	26.0	Sample not soluble		
Vinyon CF (vinyl chloride-acetate)	Croceine Scarlet MOO	Acid	80.0	10.0	9.0	0.141	0.205	1.4
Polyacrylonitrile	Croceine Scarlet MOO	Acid	63	42.5	38.0	0.112	0.144	1.3
High-acrylonitrile dynel†	Croceine Scarlet MOO	Acid	46.5	24.5	8.5	0.260	1.080	4.2
Dynel	Croceine Scarlet MOO	Acid	50	15.0	8.5	0.330	1.080	3.3
Dynel	Xylene Milling Blue BL	Acid	68.0	16.5	10.5	1.66	4.75	2.9
Orlon staple, type A-3	Xylene Milling Blue BL	Acid	71.0	32.0	7.0	Insufficient material		
Chemstrand	Xylene Milling Blue BL	Acid	72.0	25.0	12.0	1.60	4.12	2.6
Dynel	Pontamine Red 8BL	Direct	50	19.5	11.5	0.155	0.810	5.2
Dynel	Ponsol Red G2BN Paste	Vat	50	20.5	22.5*	1.45	1.95	1.34
Dynel	Celanthrene Red 3B	Dispersed	50	11.5	13.0	3.75	3.03	0.81
Dynel	Rhodamine 6GDN	Basic	50	18.5	13.5	0.90	1.32	1.5
Dynel	Solacet Fast Scarlet B-125	Soluble acetate	50	6.5	2.5	0.48	2.85	6.0
Dynel	Solacet Fast Blue 2BS	Soluble acetate	68.0	21.0	8.5	0.65	4.9	7.5
Orlon staple, type A-3	Solacet Fast Blue 2BS	Soluble acetate	71.0	54.0	6.5	Insufficient material		
Chemstrand	Solacet Fast Blue 2BS	Soluble acetate	72.0	37.5	8.0	Insufficient material		
Chemstrand	Solacet Fast Scarlet B-125	Soluble acetate	51.0	12.5	5.5	Insufficient material		
Orlon staple, type A-3	Solacet Fast Scarlet B-125	Soluble acetate	68.0	13.0	5.0	Insufficient material		

* Color dulled by copper.
† Laboratory-prepared dynel containing 60% acrylonitrile instead of the usual 40%.

TABLE II. DYEING OF DYNEL; ACID DYE, *p*-PHENYLPHENOL

	Blue-light reflectance (%)	Dye pickup: % on wt. of fiber	Dye pickup: % of control
Control (no copper)	13.5	0.330	—
Cupric oxide	15.8	0.302	90
Cupric sulfate	11.5	0.600	180
Cuprous oxide	10.0	0.700	210
Cupric acetate, Sulfoxite S	8.2	1.18	360
Electrolytic copper	9.0	1.15	350

TABLE III. REDUCED COPPER AS SOLE DYE ASSISTANT; DYNEL

	Blue-light reflectance (%)	Dye pickup: % on wt. of fiber	Dye pickup: % of control
Control (no copper, no *p*-phenylphenol)	20.0	0.125	—
p-Phenylphenol	13.5	0.330	264
Cupric acetate, Sulfoxite S	11.2	0.580	434

Sorption of Copper

To determine whether acrylonitrile fibers pick up copper from solution more avidly than non-acrylonitrile fibers, several of the samples of Table I, dyed with and without aid of copper, were analyzed for copper by means of the emission spectrograph. The results of these exploratory determinations are presented in Table IV. While they did indicate stronger sorption of copper by the acrylonitrile fibers in most cases, the concentrations involved were so low that the reliability of the data was questionable. A series of standard dyeings was therefore run on dynel using progressively higher concentrations of copper and reducing agent in the dye bath, and the various samples were analyzed for copper. The results of this series, shown in Figure 2, indicated that the amount of copper sorbed by dynel increases (but not linearly) with copper content of the bath. Another series of copper-sorption experiments was therefore run on a variety of fabrics under exaggerated but simplified conditions: the fabric samples were steeped in boiling water containing only copper (5% copper ion on fabric, instead of the 0.32% employed in normal dyeing operations) in the form of copper acetate, and zinc formaldehydesulfoxylate in the usual ratio of 0.4 part per part of copper acetate. Except in cases where supplies of material at hand were too small to permit detailed study, specimens were withdrawn after 15, 30, 60, 90, and 120 min. exposure, rinsed

TABLE IV. SORPTION OF COPPER BY VARIOUS FIBERS*

	Copper content (% as Cu)
Dynel	0.15
Orlon staple, type A-3	0.17
Chemstrand	0.11
Viscose rayon	less than 0.02
Acetate rayon	less than 0.02
Vinyon CF	0.02

* Acid dye; standard dyeing procedure, using 2.25% *p*-phenylphenol and 1% cupric acetate, 0.4% Sulfoxite S.

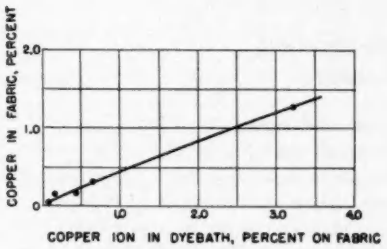


FIG. 2. *Sorption of copper by dynel fabric.*

thoroughly, and analyzed for copper. The results of these experiments, shown in Table V, clearly indicate that acrylonitrile fibers pick up copper from solution more strongly than do any of the non-acrylonitrile fibers tested, with the single exception of wool.

To determine whether there was any apparent difference in extractability of copper from acrylonitrile fibers on the one hand and from non-acrylonitrile fibers on the other, the samples that had been steeped in copper solutions for 120 min. were leached with boiling water, and specimens were withdrawn after 30, 60, and 120 min. (except, again, in cases where the supply of material was limited) and analyzed for copper. The results of these extraction experiments, presented in Table VI, show only minor differences in extraction-resistance.

The data of Tables V and VI are so numerous that in a single chart they would be confusing, and it is doubtful whether they are significant enough to justify numerous charts. To convey some idea of the shapes of the sorption and extraction curves, however, the data on cotton, dynel, Orlon staple, and wool, during both the sorption and extraction steps, have been plotted on a single chart and are presented in Figure 3.

To determine whether the actual presence of copper was required for enhanced results in dyeing, a series

TABLE V. SORPTION OF COPPER UNDER EXAGGERATED CONDITIONS (5% COPPER ION, ON FABRIC)

	Copper content of fabric (%) for steeping periods of:				
	15 min.	30 min.	60 min.	90 min.	120 min.
Cotton	0.025	0.027	0.047	0.072	0.095
Acetate rayon	0.035	0.025	0.075	0.024	0.100
Nylon	0.031	0.040	0.056	0.037	0.080
Wool	1.15	1.42	1.72	1.70	1.82
Dynel	0.16	0.28	0.44	0.64	0.61
High-acrylonitrile dynel	0.15	0.23	0.36	0.38	0.43
Chemstrand	0.75	1.24	1.44	1.50	
Orlon staple, type A-3	1.62		1.98	1.94	1.92
Polyacrylonitrile	0.17	0.22	0.60	0.43	0.43

TABLE VI. EXTRACTION OF SORBED COPPER WITH BOILING WATER

	Copper content of fabric (%) for leaching periods of:			
	0 min.	30 min.	60 min.	120 min.
Cotton	0.095	0.030	0.038	0.024
Acetate rayon	0.100	0.020	0.020	0.024
Nylon	0.080		0.024	0.060
Wool	1.82	1.90	1.76	1.70
Dynel	0.61	0.43	0.38	0.34
High-acrylonitrile dynel	0.43	0.33	0.32	0.31
Chemstrand	1.50	1.38	1.37	
Orlon staple, type A-3	1.92	1.48		1.22
Polyacrylonitrile	0.43	0.66	0.44	0.42

TABLE VII. DYEING DYNEL; COPPER PARTIALLY EXTRACTED BEFORE DYEING

Extraction period (hrs.)	Red-light reflectance* (%)
0	10.6
4	24.0
8	27.5

* Low reflectance indicates deep color.

of experiments was run in which swatches of dynel fabric were first impregnated with copper and then steeped in boiling water for progressively longer periods to leach out the copper. The samples were then dyed with Xylene Milling Blue BL, using *p*-phenylphenol but without the aid of copper. The results of this series are shown in Table VII. It was not practical to use exaggerated amounts of copper in these experiments, since all of the samples—even those that had been subjected to prolonged extrac-

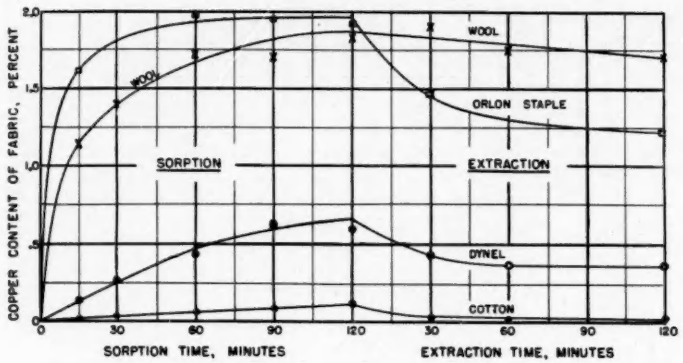


FIG. 3. *Sorption and extraction of copper.*

tion—exhausted the dye bath almost completely, and differences in dye pickup were relatively small. A "normal" copper concentration—1% of cupric acetate, on fabric—was therefore employed in the impregnation step.

Sorption of Other Metals

In the course of the early exploratory work, a wide variety of metal salts were tried in cursory fashion as dye assistants for dynel. These were included in the dye bath to the extent of 1% on fabric, and the dye employed was Xylene Milling Black 2B. The various samples prepared in the course of this work were analyzed semi-quantitatively by means of the emission spectrograph, and the results were reduced to a common basis—percent of available metal-ion take-up. These data, together with those for depth of color expressed in terms of blue-light reflectance, are listed in Table VIII. Three of the more strongly sorbed metals—copper, zirconium, and silver—were then compared more carefully at a metal-ion concentration (on fabric) of 0.32%. The results of this comparison are shown in Table IX.

TABLE VIII. SORPTION OF VARIOUS METALS BY DYNEL

	Available metal sorbed (%)	Blue-light reflectance (%)
Zirconium acetate	78	21.3
Silver nitrate	73	15.0
Stannous chloride	69	25.0
Chromium nitrate	54	27.8
Metallic copper (powder)	53	18.0
Cuprous oxide	52	14.8
Aluminum sulfate	41	24.3
Barium acetate	40	24.3
Cuprous chloride	39	5.5
Manganous acetate	28	26.3
Lead acetate	17	32.0
Cobaltic oxide	20	25.0
Metallic iron (filings)	11	29.5
Magnesium oxide	10	25.3
Calcium oxide	8	30.0
Zinc sulfate	4	25.5
Nickel(ous) acetate	<2.5	24.5
Control (no assistant)		26.0

Discussion

The use of dissolved copper in connection with the dyeing of acrylonitrile fibers has not yet been studied exhaustively enough to support any comprehensive explanation of the mechanism of the copper effect, and, in addition, the data presented herein appear to be contradictory in some particulars. Limited speculation as to the mechanism may be worth while

TABLE IX. SILVER AND ZIRCONIUM AS DYE ASSISTANTS (XYLENE MILLING BLUE BL)

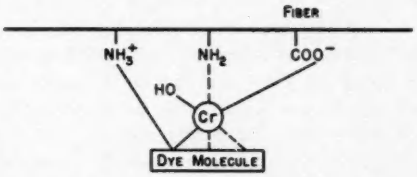
	Red-light reflectance (%)
Control	16.5
Reduced copper	10.5
Silver acetate	12.2
Silver nitrate	11.5
Silver oxide	13.0
Zirconium nitrate	18.5
Zirconium sulfate	18.8

even now, however, since it may point the way to further experimentation.

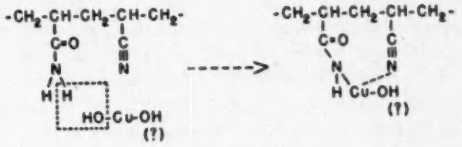
Of the several hypotheses that have come to mind to "explain" the copper effect, only one, which postulates the formation of a "bridge" between the resin molecule and the dye molecule, appears to stand up in the face of the information available. Thus, it is obvious that a mechanism of simple swelling of the molecular structure cannot explain the effect, since copper is selective, rather than general, in its action. More plausible than the "simple-swelling" hypothesis is one that postulates catalysis of hydrolysis of nitrile groups to amide or carboxyl groups, which would increase the tolerance of the resin for water and for water-soluble dyes. Acrylonitrile copolymer films exposed to copper solutions under the conditions employed in dyeing do show slightly more absorption of infrared radiation in the region attributed to carbonyl groups than do films exposed to similar conditions but minus the copper, and thus there is some evidence that copper does promote hydrolysis. Two facts argue against this as the primary mechanism, however: the fact that affinity for water-soluble basic dyes is not enhanced, and the fact that affinity for acid and direct dyes drops off if copper is leached out of the fiber. Dye affinity appears to depend upon the amount of copper actually in the fiber—not upon what the copper did to the fiber previously.

The last observation is, of course, one of the primary reasons for supposing that copper ions serve to bind dye molecules to acrylonitrile fiber molecules. The role of chromium in fixing certain dyes to wool [12] would seem to be pertinent in this connection, and it may be worth while to ignore apparently discordant evidence for the moment and explore the possibility of analogous behavior in the present case.

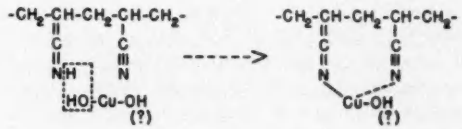
The mechanism proposed by Valko [16] to explain the effectiveness of chromium in wool dyeing postulates the formation of both direct salt linkages and coordinate valence bonds between the chromium ion, the wool molecule, and the dye molecule:



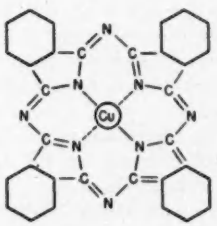
Generally speaking, similar opportunities would seem to exist for complex formation between acrylonitrile resins, copper ions, and dye molecules. Taking up first the interaction between the fiber molecule and copper, it is apparent that any amide or carboxyl groups that might be formed by hydrolysis of nitrile groups could react readily with hydrated cuprous or cupric copper:



Another possibility of the same general type is suggested by the enol structure of polymeric acrylonitrile postulated by Houtz [8]:



The possibility of coordination complexes between copper ions and nitrile groups seems plausible on the basis, first, of the familiar inorganic cupro- and cupricyanide complexes, and, second, of the familiar phthalocyanine complex [7] which can be formed between copper and a wide variety of 2,3-dinitriles:



This phthalocyanine structure suggests an elaborate analogy in which the nitrile groups on alternating carbon atoms of the main polymer chain or on neighboring chains would play the role of the 2,3-dinitrile structures above, and the five-membered nitrogen-bearing rings above would be replaced by six-membered rings.

Speculation as to possible specific complexes between copper ions and dye molecules seems hardly justified on the basis of information now available. Copper salts are known to be troublesome in connection with the dyeing of natural fibers with many acid and direct dyes, and it is not unusual to go to considerable trouble to exclude copper from dyeing operations. In this connection, it is interesting to note that while such undesirable side reactions have been observed in some cases when cupric copper was present in the dyeing of acrylonitrile fibers, reduced copper has, thus far as least, given no such trouble. This fact, together with the established superiority of reduced copper over cupric copper as a promoter, suggests the possibility of an oxidation-reduction reaction between the copper ion and the fiber molecule.

The failure of copper to enhance markedly the dyeing of either polyacrylonitrile fiber or wool, despite the fact that it is taken up to a significant extent by both, and the failure of other metals to promote the dyeing of dynel even though they appear to be taken up more or less avidly from solution, must be acknowledged in this discussion. With regard to polyacrylonitrile, it is pertinent that more extensive experiments have shown that markedly improved results are obtained as the concentration of *p*-phenylphenol is increased, deep shades being attained at concentrations of the order of 8% on fabric. The data presented above suggest that the resistance of the polyacrylonitrile structure to invasion by copper ions is not particularly high, but that in the presence of the relatively modest concentration of *p*-phenylphenol employed in this work, the larger dye molecules are unable to penetrate into the interior. This is, of course, not surprising in view of the high resistance of polyacrylonitrile resin to ordinary solvents and swelling agents.

The failure of reduced copper to enhance the dyeing of wool, and of zirconium, tin, and chromium, for example, to enhance the dyeing of dynel, must, on the basis of present knowledge, be dismissed with the comment that affinity of the fiber for a given metal ion is apparently not of itself sufficient to assure positive results in dyeing. Thus, it is entirely reasonable that the complex wool molecule, for example, should saturate all of the possible coordination valences of copper, and that dye molecules should not be held to any significant extent by any remaining electrovalences [10]. Similarly, in the case of dynel, while the effectiveness of silver as well as copper suggests that other metals of the so-called "Werner" group—zinc, cobalt, and nickel, for example—might also be effective, their apparent ineffectiveness cannot be regarded as particularly significant, at least until they have been studied much more extensively. Silver itself is of course effective enough to justify further study with a view to actual exploitation, and experiments along this line are in progress. At the present writing it does not appear to offer any advantage over reduced copper, but the work done thus far is not regarded as definitive.

Practical Considerations

Most of the experimental work done thus far on the copper technique has been done with practical goals in mind, and this technique has been recommended for the dyeing of dynel in practical operations for the past year or so [5]. In addition to the advantage of its making possible deeper shades than can be obtained by any other practical method, the copper effect makes possible the elimination of *p*-phenylphenol in cases where the deepest shades are not required or where *p*-phenylphenol is regarded as undesirable. On the basis of extensive tests, it appears that copper does not impair the outstanding washfastness of dyed dynel, nor its remarkable resistance to hypochloride bleach solutions. Light-stability, on the other hand, does appear to be affected in some cases when copper is used as a dye assistant, but not always adversely. In about as many cases as it is detrimental to light-stability, copper has been found to improve light-stability, sometimes markedly. This study is complicated by the fact that both dyed and undyed dynel withstand natural sunlight far better than they withstand radiation in a Fadeometer or other accelerated-aging device, and by the extremely poor correlation in the case of dynel between Fadeometer results and results of aging in natural sunlight.

Further research is being done on both the theoretical and the practical aspects of the copper technique for dyeing acrylonitrile fibers, and revised procedures are recommended as the technique is improved and simplified [6]. According to recent reports [9], work on Orlon has been carried out along lines similar to those followed in connection with dynel and Vinyon N, and other acrylonitrile fibers are doubtless receiving similar attention. For the present, the most fruitful line of activity seems to be

detailed study of individual dyes in connection with specific acrylonitrile fibers, but progress on a broader front can be expected as more knowledge about the mechanism of the copper effect is accumulated.

Acknowledgments

The authors wish to acknowledge their indebtedness to many of their colleagues in the laboratories of Carbide and Carbon Chemicals Company for their help in connection with this project; and to acknowledge particularly the valuable contributions of Mr. A. G. Schoonover, Mr. J. H. Purse, and Mr. J. W. Kearns.

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A New Method for Raw-Wool Scouring and Grease Recovery*

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Introduction

The operation of scouring raw wool is the first and one of the most important steps in the processing of wool. The process demands extreme care; otherwise, the ultimate quality of the wool is jeopardized. Damage incurred in scouring may affect carding, combing, spinning, weaving, and dyeing, and thus affect ultimate wearing quality.

Raw wool is contaminated with 40% to 70% of extraneous matter, of which 5% to 20% is suint, 10% to 40% is "grease" (more correctly, wax), and the remainder is sand, dirt, vegetable matter, urine, and fecal matter. The primary objective in scouring is the removal of these impurities, leaving a white, nonfelted, ash-free product that contains around 0.5% of residual grease.

Wool suint is generally regarded as water-extractable material, presumably secreted by the sweat glands of the animal. It consists, in part, of a mixture of potassium soaps of fatty acids, ranging from valeric to palmitic acids [6]. In addition, suint contains minor amounts of lactic, hippuric, and succinic acids, urea, and lanaurin, a bile pigment derivative which imparts the reddish-brown color to an aqueous solution of suint [23].

The greasy material in wool is secreted through the sebaceous glands of the animal. It is principally a mixture of waxes, consisting of the esters of several high-molecular-weight monohydric alcohols with fatty acids [7]. The component alcohols consist of three major series: the sterols, principally cholesterol; the triterpene alcohols, closely related to the sterols; and the higher aliphatic alcohols. The component wool wax acids consist of four major series: the normal fatty acids; the hydroxy acids; the ante-iso acids; and the iso acids [32].

Two methods are commonly employed for the scouring of raw wool: the aqueous soap- or detergent-soda ash process and the solvent process. Of these, the aqueous method is by far the more common. The scouring process is carried out in a long train consisting of four to six separate bowls through which the wool is carried with a gentle mechanical action. Soap or synthetic detergents and soda ash, added in varying amounts to all bowls except the final rinse bowl, perform the major scouring action. Conventional aqueous scouring practice is slow and requires much space; there is danger of alkali damage to the fibers; and the considerable felting which invariably occurs leads to increased fiber breakage in the subsequent carding operation [34].

Solvent extraction offers an alternative method of cleaning raw wool, yielding a degreased product with little fiber damage, minimum felting, and ready recovery of grease. A subsequent rinse in water is invariably required to remove the suint and dirt. A batch-extraction process utilizing petroleum naphtha as the solvent has been successfully operated in this country for over 50 years. More recently, there has been considerable interest in the development of equipment [4, 11] for the continuous degreasing of raw wool with trichloroethylene as the solvent. Although the solvent procedure offers features which are desirable, the general acceptance of the method has been slow, chiefly because of economic considerations, industrial hazards from toxicity of escaping vapors, and inflammability of some solvents.

Although scouring costs have not been considered excessively high, it is generally agreed that there is need for improvement in scouring methods. There is need for milder treatments and treatments leading to less felting with consequent less fiber breakage in

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† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

carding. There is also need for speeded-up processing and for a process requiring less space.

But perhaps the most immediate problem facing the wool-scouring industry—indeed, the wool industry as a whole—is the means of disposal of effluent. Wool-scouring wastes are among the most objectionable types produced by industry. For the most part, they are dumped directly into streams. The contamination and resulting putrefaction lead to most disagreeable odors, and the extremely high B.O.D. of the effluent imposes a heavy pollution load on the stream.

With the growing realization that water supplies are definitely limited, the wool industry is forced to consider either appropriate treatment of the waste water or new methods of scouring in which there is no effluent-disposal problem. All grease-recovery systems are expensive. Furthermore, the potential market for the grease is limited and unpredictable; hence, less than 10% of the potentially available grease is recovered.

Solvent recovery has been suggested as a solution. However, whereas solvent extraction does recover grease, it also leaves the objectionable suint salts which must subsequently be removed in a backwashing operation and then discarded. Apparently, the removal of grease has little if any effect on reducing the B.O.D. of the backwashing waste [16].

The primary objective of the present investigation of the raw-wool scouring process has been to evaluate some of the underlying physicochemical principles involved in the cleaning operation as the basis for possible improved technical practice. These studies are directed toward the effect of the scouring treatment on fiber properties, as well as the problems of effluent disposal and grease recovery.

As a first consideration, the role of suint in the scouring process was investigated. The detergent properties of suint salts in scouring are recognized; however, it appears that suint salts have never been used to their fullest effectiveness. The Duhamel scouring process [5], developed in France, is based on the use of a water extract of suint. The raw wool is first steeped in hot water to dissolve the suint. This suint solution is continuously clarified of grease and dirt by centrifuging, and is then returned to the first two bowls and used as the major scouring agent. In modern practice, the recovered aqueous suint solution is fortified by the addition of controlled amounts of soap or synthetic detergent and alkali.

The results of the present investigation indicate that the emulsifying power of suint is enhanced markedly by the addition of alcohol and salt. Moreover, the emulsified grease can be separated and recovered from the scouring waste by a small increase in the alcohol concentration. These principles are the basis for a new process for the neutral scouring of wool, with simultaneous recovery of grease, removal of dirt, and recycling of the alcohol, suint, and other detergent additives. They have been applied experimentally in laboratory-scale continuous scouring operation.

Experimental Procedure

In the development of a laboratory procedure for the investigation and evaluation of factors involved in the scouring of raw wool, the principal consideration was to adopt a method of testing which would simulate as closely as possible the operating conditions in commercial scouring practice.

Two standard test procedures were employed in the present studies. The first method, the single-scour beaker test, is a standardized procedure in which wool is scoured in 500-ml. beakers immersed in a 60°C constant-temperature bath. A single 3-g. sample of raw wool is scoured in two successive 400-ml. portions of the scouring solution for 3 min. in each beaker. Agitation of the scouring solution is provided by a glass weight attached to a short arm on a windshield-wiper motor. After scouring, the sample is rinsed thoroughly in distilled water at room temperature, and dried in an oven at 100°C to constant weight. The residual-grease content of the scoured sample, determined by Soxhlet extraction with an organic solvent, serves as the basis for comparison of the effectiveness of various scouring procedures.

The second test method is a cumulative scouring procedure similar to that described by Leonard and Winch [15] as a quantitative test for the evaluation of wool-scouring detergent systems. Stainless-steel 8-l. beakers serve as the scouring bowls. A specially constructed constant-temperature bath maintains the temperature of scouring, which is 60°C. Four motor-driven wringers, mounted permanently above the constant-temperature bath in juxtaposition to the scouring bowls, serve as the squeeze rolls for the individual bowls. For agitation, an up-and-down motion is imparted by means of a flat, perforated, stainless-steel disk attached by a slender rod to the arm of a windshield-wiper motor. The scouring operation

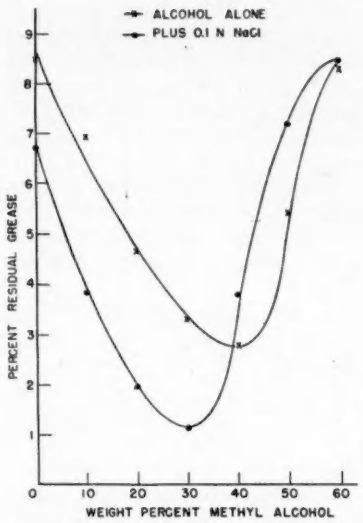

FIG. 1. *The scouring of raw wool in solutions of methyl alcohol with and without added sodium chloride.*

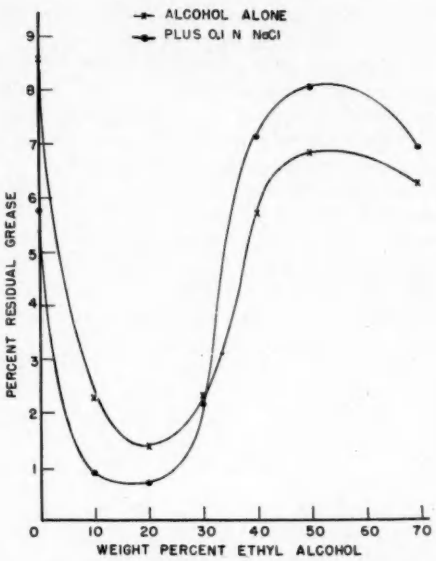

FIG. 2. *The scouring of raw wool in solutions of ethyl alcohol with and without added sodium chloride.*

consists of feeding a series of 10-g. samples of grease wool in a loose carded form through the first bowl and squeeze roll, onto the second bowl, and so on, through the system. The time of immersion in each bowl is 3 min. The scoured samples are thoroughly rinsed in distilled water, dried, and extracted.

For use as a standard wool, a large lot of medium California wool was opened and blended in an experimental-type opener [33]. The opened wool was placed in a closed container and stored in a cold room at 4°C to minimize any aging effect which might alter the scouring characteristics. For the scouring trials, small portions were further homogenized by repeated hand-carding and mixing. This standard wool in the carded form had a shrinkage of 33%, consisting of 10% grease, 9% suint, and 14% dirt, on the basis of the grease wool.

Analytical-grade reagents were used in all cases unless otherwise stated. All solutions were made up with laboratory distilled water.

Results

With the single-scour beaker test method, a study was made of the effect of added water-soluble alcohols and salts on the scouring efficiency. Figures 1 to 6 are representative of the experimental results obtained for the homologous series of primary straight-chain alcohols, from methyl to hexyl, obtained by scouring the standard raw wool at varying alcohol concentrations with and without added 0.1*N* sodium chloride. Although no alkali was added, the scouring solutions were slightly basic (pH 7.5) because of the dissolved suint. The reported residual-grease values are based on the oven-dry weight of the scoured wool.

Analysis of the curves reveals several significant points that are common to the effects produced by the water-soluble alcohols examined. As the alcohol concentration is increased, there is an initial decrease in the residual-grease content to a minimum value; further addition of alcohol causes a sharp rise in the residual-grease content; and, finally, with the completely water-miscible alcohols at higher concentrations, a gradual decrease takes place. With the incompletely miscible alcohols—butyl, amyl, and hexyl—phase separation occurs before a maximum in the curve is observed. The value of the residual-grease content at the minimum decreases progressively from methyl to butyl and then increases. The presence of added sodium chloride enhances the scouring power of the alcohols at the lower concentrations;

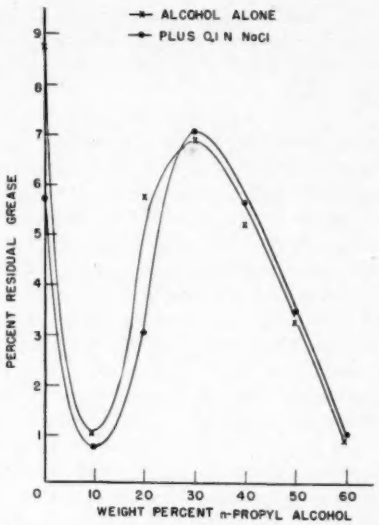

FIG. 3. *The scouring of raw wool in solutions of n-propyl alcohol with and without added sodium chloride.*

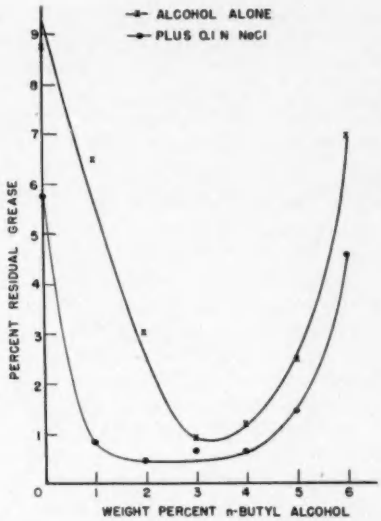

FIG. 4. *The scouring of raw wool in solutions of n-butyl alcohol with and without added sodium chloride.*

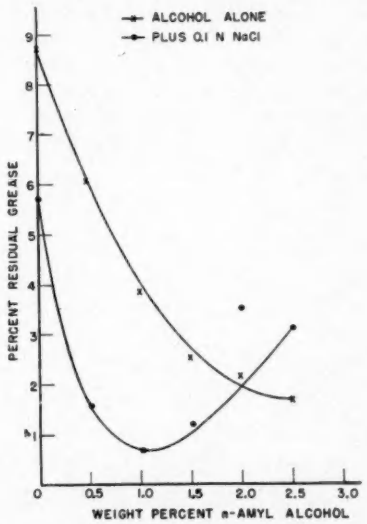

FIG. 5. *The scouring of raw wool in solutions of n-amyl alcohol with and without added sodium chloride.*

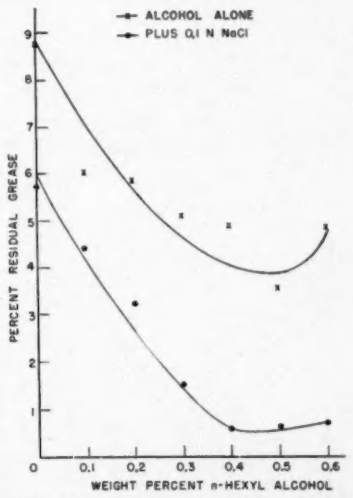

FIG. 6. *The scouring of raw wool in solutions of n-hexyl alcohol with and without added sodium chloride.*

however, at alcohol concentrations beyond the minimum a reverse effect is observed. Detailed interpretation of these observations is presented in the Discussion section.

That the improvement in scouring resulting from the addition of alcohol at the lower alcohol concentrations is dependent upon the presence of the natural suint in wool is substantiated by the scouring of desuinted wool. (The raw wool is desuinted by steep-

ing in water at room temperature.) With the removal of suint before scouring, the building action of the alcohol disappears, as is shown rather conclusively in Figure 7 for butyl alcohol.

Other similar polar-nonpolar organic compounds such as *iso*-propyl alcohol, *iso*-, secondary, and tertiary butyl alcohol, acetone, methyl ethyl ketone, methyl cellosolve, phenol, benzyl alcohol, cyclohexanol, etc., were investigated, and results similar to those for the primary aliphatic alcohols were obtained. The addition of glycols or glycerols has no beneficial effect.

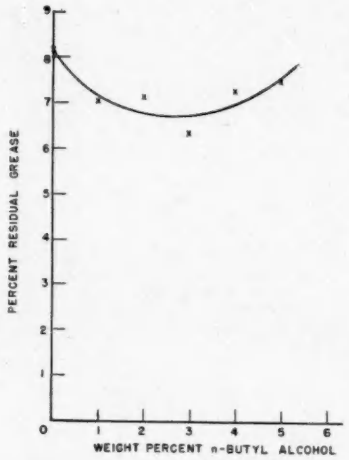

FIG. 7. *The effect of prior desuinting on the efficiency of grease removal in solutions of* n*-butyl alcohol.*

In the alcohol runs presented above, the concentration of the added sodium chloride was held constant at 0.1*N* in all cases. The effect of the addition of varying amounts of sodium chloride in the presence of a constant concentration of butyl alcohol (2% by weight) is shown in Figure 8. Although the change in scouring efficiency is small, there is an optimum concentration at about 0.1*N* salt. Even in the absence of alcohol, sodium chloride improves the extent of grease removal, as illustrated in Figure 9. As in the case of the alcohol, removal of suint before scouring nullifies the effect of salt—that is, the increased scouring efficiency is due to the synergistic interaction between the salt and suint. Other neutral alkali-metal salts show a similar behavior. When added in ion-equivalent amounts, the order of effectiveness of those studied was $Na_2SO_4 = NaI > NaCl = NaBr = NaNO_3 = K_2SO_4 > NaF$.

While the residual-grease content determined by solvent extraction is the accepted index for determining the efficiency of scouring, conclusions based on this factor alone may at times be misleading. This is illustrated in Figure 10, where the residual-ash content, determined by igniting the scoured samples in a muffle oven at 600°C, is plotted as a function of

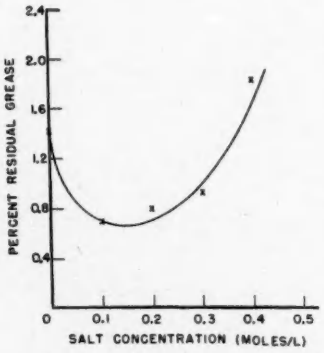

FIG. 8. *The effect of sodium chloride concentration in a 2% (by weight)* n*-butyl alcohol solution on the scouring of raw wool.*

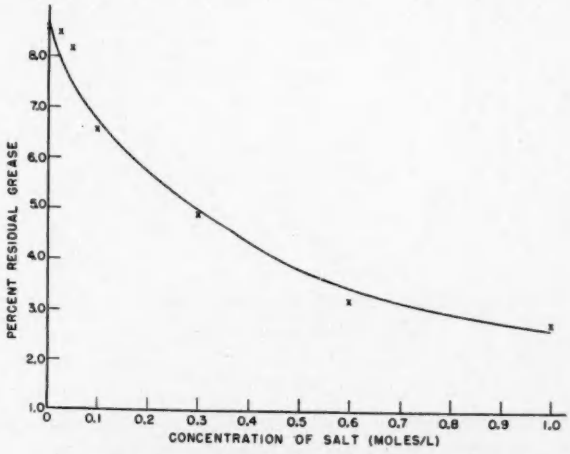

FIG. 9. *The scouring of raw wool in aqueous sodium chloride solutions.*

methyl alcohol concentration, with and without added sodium chloride. Figure 11 shows the effect of sodium chloride alone on residual-ash content. In both instances there is a definite trend toward a higher ash content with increasing concentration. A control experiment with clean wool showed that the increase in ash content in the case of sodium chloride addition cannot be attributed to the incomplete removal of the salt in the rinse operation. This divergent effect of added alcohol and added salt on the displacement of grease and dirt from wool emphasizes that the removal of these two components occurs by separate mechanisms.

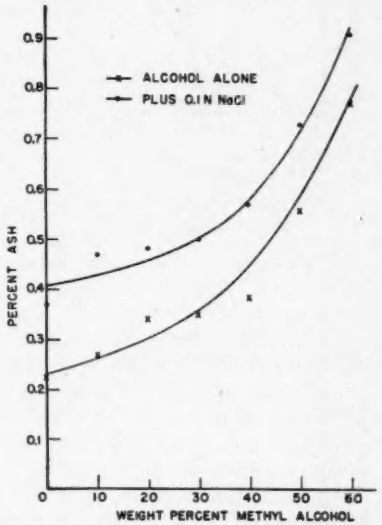

FIG. 10. *The effect of methyl alcohol concentration, with and without added sodium chloride, on the residual-ash content.*

Figure 12 shows the effect of the hardness of water (expressed as parts per million of calcium carbonate) on the scouring efficiency of the alcohol-suint-salt system. The trial was conducted with butanol, at a constant concentration of 2% by weight, and 0.1*N* salt solution, to which the required hardness was introduced as calcium chloride. The pronounced adverse effect of calcium is due undoubtedly to the formation of insoluble calcium suint salts, as encountered in the case of ordinary soap. Other alkaline-earth and heavy-metal salts have a similar effect.

The addition of alkali to the alcohol-suint system results in an improvement in scouring which is independent of a salt effect. This improvement is due to the conversion of the free fatty acids in the wool grease to the corresponding soap. Under acidic conditions, the alcohol-suint solution is totally ineffective.

The effect of temperature on the scouring efficiency of a 2% butanol plus 0.1*N* salt solution is illustrated in Figure 13. The decrease in grease removal below 40°C is reconciliable with the fact that wool grease is a solid below this temperature region.

An investigation was made of the scouring behavior of raw and desuinted wool in an aqueous soap solution with added butanol. The soap used was so-

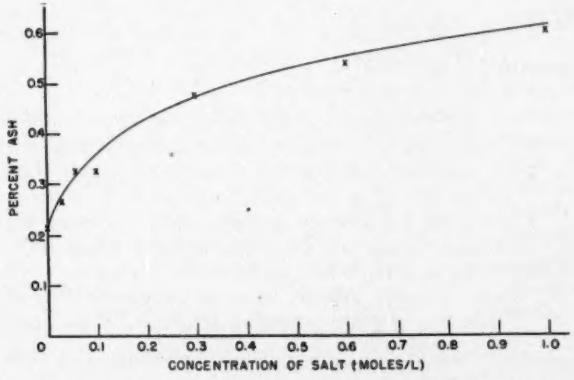

FIG. 11. *The effect of sodium chloride concentration on the residual-ash content.*

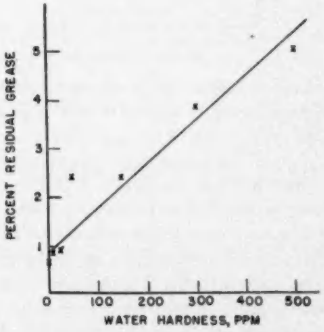

FIG. 12. *The effect of water hardness on the scouring efficiency in solutions containing 2% (by weight) n-butyl alcohol and 0.1 N sodium chloride.*

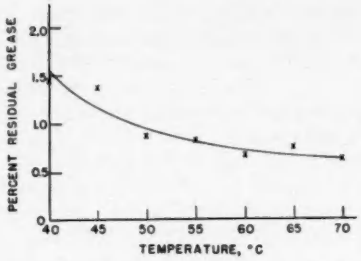

FIG. 13. *The effect of temperature on the scouring efficiency in solutions containing 2% (by weight) n-butyl alcohol and 0.1 N sodium chloride.*

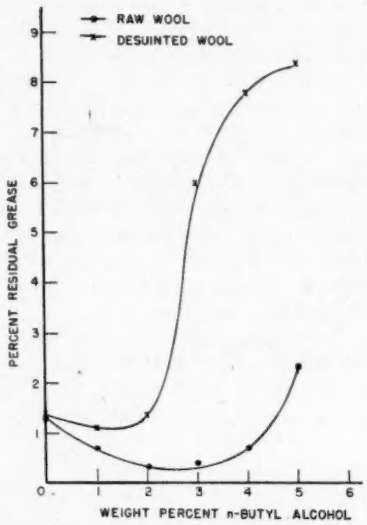

FIG. 14. *The scouring of raw wool and desuinted wool in solutions of n-butyl alcohol with 0.05% sodium stearate.*

dium stearate (J. T. Baker, U.S.P. grade). At a constant soap concentration of 0.05% by weight, there is a marked difference in the scouring efficiency *vs.* butanol concentration curves (Figure 14), depending upon whether the raw wool was initially desuinted or not. In the case of raw wool, the soap aids the scouring action of the suint and improves the grease removal (compare with Figure 4 for the effect of butyl alcohol alone). If the suint is removed by prior desuinting, the building action of the butanol disappears; at concentrations above 2% the added

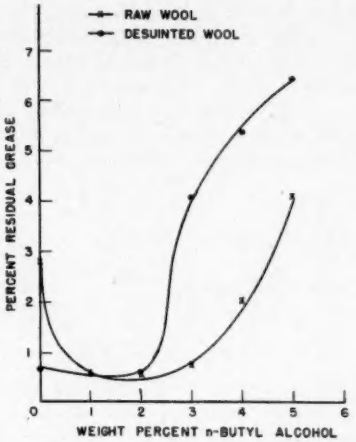

FIG. 15. *The scouring of raw wool and desuinted wool in solutions of n-butyl alcohol with 0.05% Duponol C.*

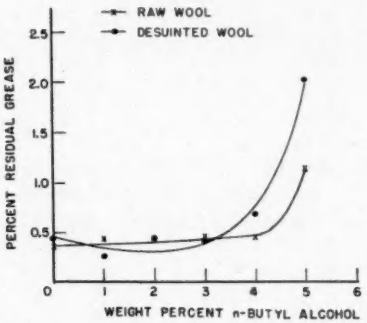

FIG. 16. *The scouring of raw wool and desuinted wool in solutions of n-butyl alcohol with 0.05% Antarox A-180.*

butanol is detrimental to the function of the soap as a detergent. A behavior similar to that of soap was observed for Duponol C,* an anionic detergent (Figure 15). The data plotted in Figure 16 for Antarox A–180,† a nonionic detergent, show a different result. In this case the presence or absence of the suint has very little effect on the scouring behavior.

The data presented up to this point were obtained by the single-scour beaker procedure, which gives

* Kindly supplied by E. I. du Pont de Nemours & Company.

† Kindly supplied by Antara Products Division, General Aniline & Film Corporation.

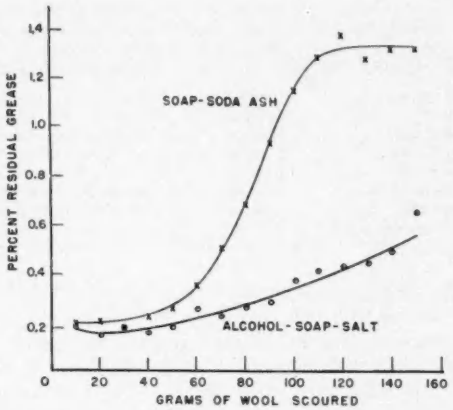

FIG. 17. *A comparison of the cumulative scouring of raw wool by the soap-soda method and by the alcohol-soap-salt method.*

a measure only of the effectiveness of a fresh solution. Since raw-wool scouring is a continuous process, it is important to evaluate the rate of exhaustion of different scouring formulations on a cumulative scouring basis in which increasing amounts of wool are scoured in the same bath. A comparison on this basis between the soap-soda method and the alcohol-suint method is shown in Figure 17. The initial compositions of the scouring bowls for the two methods are summarized in Table I.

In the case of the alkali scour (Figure 17), the residual-grease level remains fairly constant up to around 60 g., at which point the curve rises rapidly, indicating that the cleaning power of the solution has become exhausted. In the case of the alcohol scour, the residual-grease level is below that of the alkali; furthermore, the rise in residual-grease content as successive samples were scoured is more gradual, indicating that the rate of exhaustion is much slower.

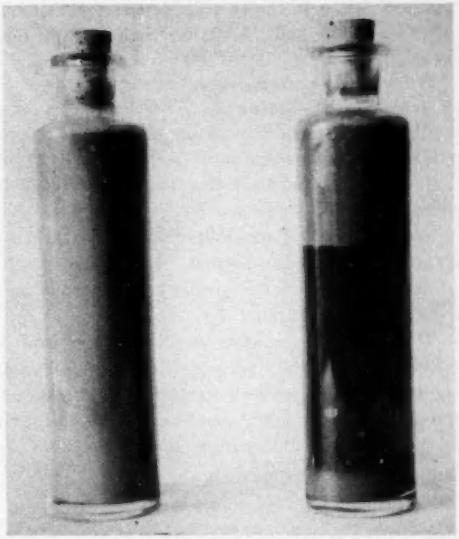

FIG. 18. *Samples of wool scouring waste.* Left—*Raw waste before treatment.* Right—*After addition of n-butyl alcohol in an amount sufficient to saturate.*

At a residual-grease content level of 0.6% it is seen that in the presence of added butyl alcohol about two times as much wool can be scoured.

Another important feature of alcohol addition is the marked effect of higher alcohol concentrations on the stability of waste-scouring emulsions. As an example, it was observed that upon the addition of butyl alcohol to a scouring waste in an amount just sufficient to form a separate alcohol-rich layer (about 7% by weight) at 60°C, rapid coalescence of the grease emulsion occurred. On allowing the solution to stand for a short period of time, a grease-rich layer collected on the surface and a dirt-rich layer on the bottom, leaving a nearly clear amber-colored mother

TABLE I. INITIAL BOWL COMPOSITION*

	Bowl No. 1		Bowl No. 2	
	Soap-soda	Soap-alcohol	Soap-soda	Soap-alcohol
Sodium carbonate	0.5%(w)	—	—	—
Sodium stearate	0.05%(w)	0.05%(w)	0.025%(w)	0.025%(w)
Sodium chloride	—	0.1*N*	—	0.1*N*
Butyl alcohol	—	3%(w)	—	3%(w)
Volume	2 l.	2 l.	2 l.	2 l.

* Bowl No. 3 consisted of a rinse in distilled water at room temperature.

liquor. Figure 18 shows a comparison of the scouring waste before and after the addition of excess butyl alcohol.

A further investigation was made into the action of other alcohols as emulsion-breaking agents. A summary of the concentrations required and the nature of the sediment is given in Table II.

The concentrations of the first five alcohols required to break the emulsion correspond with those at which the lowest scouring efficiency is reached in the results reported in Figures 1 to 6. The direction of sedimentation of the grease layer depends upon the density of the solution.

This observed emulsion-breaking property of alcohols at the higher concentration is of particular significance, for it offers a method of regeneration of the spent scouring solution and recovery of the grease in the alcohol-suint scouring process described below.

TABLE II. ALCOHOLS AS EMULSION-BREAKING AGENTS

Alcohol	Concentration	Nature of sediment
Methyl	60%(w)	Dirt and grease settled
Ethyl	40%(w)	Dirt and grease settled
n-Propyl	30%(w)	Dirt and grease settled
n-Butyl	2-phase	Grease layer on surface
n-Amyl	2-phase	Grease layer on surface
n-Hexyl	2-phase	Grease layer on surface
n-Octyl	2-phase	No flocculation observed
Propylene glycol	50%(w)	No flocculation observed

Discussion

The interaction between suint and alcohol which produces the results reported above may be interpreted either by an analysis of the interfacial relationships involved or by a consideration of the effect of alcohols on micelle structure. Discussions of the effects produced by polar additives upon the properties of surface-active solutions have recently appeared in the literature [10, 13].

The known active components of suint are similar in structure to ordinary soaps or detergents. These compounds are characterized by a charged, polar, or water-compatible, head and a long-chain, nonpolar, or oil-compatible, tail. By virtue of this structure, it is reasonable to expect that suint ions, like other surface-active agents, are concentrated and oriented at an oil-water or an air-water interface. This behavior is demonstrated by the lowering in surface tension of a suint solution [28]. Furthermore, in the solution proper, under suitable conditions of concentration, temperature, pH, ionic strength, and dielectric constant, suint ions apparently aggregate to form micelles in much the same fashion as do other surface-active agents. The colloidal nature of suint in an aqueous solution is confirmed by sedimentation diagrams obtained in the ultracentrifuge [31].

It may be postulated that at low concentrations the added alcohols influence grease removal by phase partition, presumably through transfer of the alcohol together with suint ions from the bulk phase to an interface. If emulsification is the basic factor in scouring, then the interface to be considered is that of the emulsified grease droplet. The most recent views on the role of interfacial films in the stability of emulsions have been those of Schulman and coworkers [25, 26, 27]. It has been found that for an oil-in-water emulsion of maximum stability, two emulsifying agents are necessary—one which is preferentially water-soluble and the other preferentially oil-soluble. Aickin, in a study of the detergency toward oil-soiled wool of a series of secondary fatty sulfates in the presence of added higher alcohols, has interpreted his results on the basis of the above theory [1].

If solubilization is a factor in detergency, then attention must be directed to the suint micelle-solution interface. McBain [17] has defined solubilization as the spontaneous passage of a water-insoluble substance into an aqueous-soap or detergent solution to form a thermodynamically stable solution. This type of solubility involves the incorporation of the substance within the hydrocarbon core of the micelle. With regard to raw-wool scouring, these processes probably coexist, although emulsification is probably the predominant process.

Emulsification and solubilization are phenomena which are associated with the stability of the grease in the solution proper. Of equal importance are those factors which are involved in the transfer of the grease from the fiber surface into the solution proper. This step in the detergency process is best considered by an account of the grease-solution, solution-fiber, and grease-fiber interfacial free-energy relationships.

In a thermodynamic analysis, the exact mechanism of interaction is irrelevant, and the relationship between bulk alcohol concentration, C_b, and surface

alcohol concentration, C_∞ may be expressed as

$$\underset{C_b}{\text{Bulk}} \rightleftharpoons \underset{C_s}{\text{Surface.}} \qquad (1)$$

At equilibrium,

$$K = \frac{C_s}{C_b}, \qquad (2)$$

and the corresponding free-energy change, ΔF^o, accompanying this bulk-to-surface transfer will be

$$\Delta F^o = -RT \ln \frac{C_s}{C_b}. \qquad (3)$$

For various homologous series it has been observed [14] that the energy of adsorption is a linear function of the chain length:

$$\Delta F^o = A + Bn, \qquad (4)$$

where n is the number of carbon atoms in the hydrocarbon chain, and A and B are constants. The value of ΔF^o for homologous aliphatic compounds is generally around 600–800 cal. per mole CH_2 group. This behavior is an expression of the familiar Traube's rule.

For a homologous series at equal molar concentrations, C_b equals a constant and, accordingly, from equations (3) and (4):

$$C_s = \text{constant} \pm \frac{Bn}{RT}. \qquad (5)$$

In order to test the above considerations in terms of the results obtained for the scouring of raw wool at varying alcohol concentrations, we shall assume that at the same degree of grease removal for two successive members of the homologous series—that is, at

$$g_n = g_{n+1}, \qquad (6)$$

the activities, α, of the adsorbed alcohols are equal:

$$\alpha_n = \alpha_{n+1}. \qquad (7)$$

But since the activity may be considered in the limiting case to be proportional to the concentration,

$$\alpha_n = K'_n C_n, \qquad (8)$$

then

$$K'_n C_n = K'_{n+1} C_{n+1}. \qquad (9)$$

Upon rearrangement and combination with equation (3), the following relationship is derived:

$$\frac{C_n}{C_{n+1}} = \frac{K'_{n+1}}{K'_n} = K = \exp \frac{\Delta F_n - \Delta F_{n+1}}{RT}. \qquad (10)$$

This may be expressed in logarithmic form as

$$\ln C_n - \ln C_{n+1} = \ln K = \frac{\Delta F_n - \Delta F_{n+1}}{RT}. \qquad (11)$$

Since the free-energy change is a constant for a unit increase in n (equation (4)), the general expression for the nth member of the series becomes

$$\ln C = -n \left(\frac{\Delta F_n - \Delta F_{n+1}}{RT} \right). \qquad (12)$$

In other words, in a plot of the logarithm of alcohol concentration to give the same residual-grease content *vs.* the number, n, of carbon atoms (or CH_2 groups) of the alcohol, the theory predicts a linear decrease. From the slope of this plot, the free-energy difference would be obtained by dividing by RT.

Arbitrarily selecting a residual-grease value of 2%, the corresponding molar alcohol concentration for the homologous primary alcohol series required to reduce the residual grease to this level (from the data shown plotted in Figures 1 to 6) is plotted on a semilogarithmic scale as a function of the number

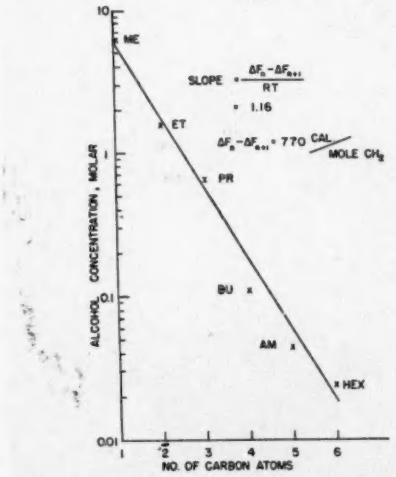

FIG. 19. *The relationship between the concentration of initially added alcohol required to reduce the residual grease to 2% and the chain length of the alcohol.*

of carbon atoms in Figure 19. Significantly, the linear decrease is observed in accord with the relationship expressed above in equation (12). Also, the change in the free energy of adsorption per CH_2 group as determined in the experimental plot is 770 cal. per mole CH_2, in surprisingly good agreement with the value of 600–800 cal. derived from surface-tension data.

This analysis lends support to the view that the initially added alcohol is involved in a surface phenomenon rather than in true solvent action.

An alternative consideration is the role of micelle formation in the over-all picture of grease removal from wool. Whether the colloidal aggregrate or the long-chain ion of a soap or detergent is the active constituent of a detergent bath is subject to conjecture [19].

The effect of alcohol addition on the critical concentration for micelle formation (CMC) of dodecylammonium chloride, determined by the dye-titration method of analysis, has shown that the added alcohols lower the CMC, and the decrease per mole of alcohol continues with lengthening of the hydrocarbon chain [2]. The interpretation is that alcohols and other polar-nonpolar compounds form a new type of micelle in which the polar-nonpolar molecules align themselves between the soap molecules, with polar heads oriented out [8, 9].

The observed increase in grease-removal efficiency with the initial addition of alcohol may be interpreted by the thesis that a lowering of the CMC is accompanied by an increase in detergent action. The effect of salts in lowering of the CMC of solutions of anionic detergents [3, 12, 18] is undoubtedly a factor in the improved detergency of such solutions.

The subsequent decrease in scouring efficiency which is apparent upon the further addition of alcohol may be also reconciled with the effect of alcohol on micelle structure. Ward [30] has shown by conductance measurements that in the case of sodium dodecyl sulfate, micelles are no longer evident in an aqueous ethyl alcohol solution above 40% by weight concentration. Similar studies of dodecylammonium chloride in water-organic solvent systems indicate that there is a transition from a colloidal aggregate to an ordinary electrolyte as the percentage of organic addend is increased [20, 21, 22].

This disappearance of colloidal properties at an intermediate alcohol concentration may be advanced as an explanation of the emulsion-breaking properties of added alcohol at these concentrations. Finally, in the case of the lower and completely water-miscible alcohols, the marked decrease in residual grease at higher concentrations is undoubtedly attributable to the true solvent action of the alcohol on grease.

Application

The foregoing results, obtained by beaker-scale studies, show promise of possible practical application in a process combining the scouring of raw wool under neutral conditions together with the clarification of the effluent wastes and recovery of the grease. In order to develop the process and to obtain significant information for application to possible pilot-scale studies, a laboratory-scale, all-glass, continuous-flow apparatus was designed. In these preliminary studies, *n*-butyl alcohol was selected for detailed investigation because of the relatively low concentration required for scouring, and because butyl alcohol functions more satisfactorily in emulsion-breaking than do the higher alcohols.

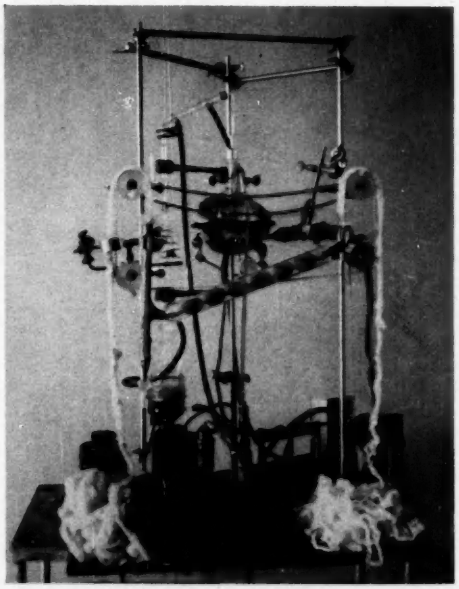

FIG. 20. *Continuous-flow laboratory assembly for the study of alcohol-suint scouring process.*

Description of Apparatus

A photograph of the assembly is shown in Figure 20, and a flow diagram in Figure 21. The scouring chamber, which has a capacity of 200 ml., consists essentially of an ordinary bulb-type laboratory condenser modified to provide inlets and outlets for both the wool and the scouring solution. To facilitate the sedimentation of the heavier dirt particles, the chamber is mounted at an angle. The extension of the lower end serves as a dirt-collecting sump from which the accumulated dirt is discharged periodically by means of stopcock *A*. The temperature of scouring is controlled by circulating water from a constant-temperature bath through the jacket surrounding the chamber.

The grease wool, in a carded, sliver form, is introduced into the left end and is passed through the scouring chamber in counter-current flow to the scouring solution by means of a stainless-steel ladder chain. Short lengths of stainless-steel wire spot-welded along the chain engage the wool, facilitating its passage through the chamber. Mechanical agitation during scouring is produced by a special drive mechanism which imparts an oscillating advancing motion to the chain. The feed rate of raw wool can be varied from approximately 1 to 3 g. per min., and the corresponding average time of immersion in the scouring solution is from 3 to 1 min. The ratio of solution to raw wool is approximately 100 : 1.

In operation, fresh scouring solution containing recovered suint in a 3% (by weight) butyl alcohol solution is fed from the boiler of the alcohol-recovery still through a glass-wool filter into the right end of the scouring chamber. The effluent scouring waste is withdrawn from the left end into a waste receiver consisting of a calibrated tube fitted with stopcock *B*, which is closed when the flow rate is being measured. The reclaimed butyl alcohol from the recovery still is collected in the distillate receiver, which is similar in construction to the waste receiver. Since the alcohol distillate is a two-phase liquid system, an indication of the rate of distillation is obtained by closing stopcock *C* and observing either the rate of flow or the relative volume of the alcohol-rich and water-rich layers.

During operation of the system, stopcocks *B* and *C* are open, and the scouring waste and recovered alcohol flow directly into the clarification unit. The added butyl alcohol raises the concentration in the solution to the saturation point, causing the dirt and grease to coalesce and separate into a top grease-rich layer and a bottom dirt-rich layer, leaving a clear reddish-brown solution between, which contains water-soluble suint and sodium chloride. The clarification chamber is jacketed to permit temperature control of this stage of the process.

A piston-type circulation pump, located at the lowest point in the apparatus, draws the clarified solution (containing salt and suint in a saturated

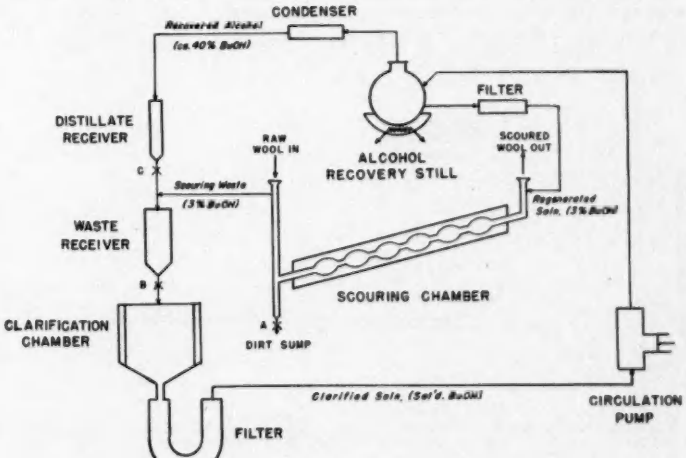

FIG. 21. *Flow diagram of laboratory assembly for alcohol-suint scouring process.*

butyl alcohol solution) upward through a glass-wool filter and feeds it into the alcohol-recovery still located at the highest elevation in the system. Flow through the remainder of the apparatus is by gravity, and hence the rate of circulation is easily controlled by alteration of the stroke of the pump.

The various units are interconnected by transparent plastic tubing. The still is heated by an electric heating mantle controlled through a rheostat.

Procedure

The wool used in this phase of the investigation was taken from the skirted fleece of a California-grown Romeldale. The fleece was opened and blended in the experimental opener, and was then carded, in the grease state, by means of a sample machine card. The resultant web from the card was manually condensed into a sliver. This grease wool in the carded form had a shrinkage of approximately 33%, consisting of 13.3% suint, 10.1% grease, and the remainder dirt, vegetable matter, moisture, etc.

The scouring apparatus is charged initially with a distilled-water solution containing 0.5% (by weight) of sodium chloride. The over-all liquid hold-up of the system is 1.5 l. Sufficient butyl alcohol is added to the clarification chamber to produce a saturated solution. The circulation pump is then adjusted to give the desired flow rate, and the rate of distillation is set to give a 3% solution in the bottom feed to the scouring chamber.

After equilibrium conditions are established, the wool is fed manually into the inlet end, and the clean, scoured wool is removed. The scoured wool is rinsed several times before drying and extracting to determine the residual grease.

Results and Discussion

A series of scouring tests, all at 60°C and 3% alcohol, was conducted at varying solution-to-wool flow rates in order to determine the effect of this variable on scouring efficiency. The suint concentration gradually increased during the course of the tests; however, as pointed out below, this factor is of minor importance. Figure 22 shows that within the limitations of the apparatus the grease-removal efficiency is nearly independent of the relative flow rates of scouring solution to raw wool. The cut-off point indicated by the vertical dotted line marks the point at which the input scouring solution is carried out entirely by the outgoing scoured wool. The amount of solution carried out by the scoured wool is unusually high because no provision was made to squeeze the solution from the wool.

Even with adequate squeezing, the butyl alcohol carried out by the wool would still represent a major loss unless provisions were made for recovery. The simplest means of recovery would be by a backwashing operation in which fresh water is fed countercurrently to the wool, stripping the alcohol by dilution or displacement. The efficiency of such an operation would be determined by the design of equipment, which is beyond the scope of this investigation.

The extent of adsorption of the solute is an important factor in the success of the backwashing operation. Speakman [29] reported that the amount of alcohol adsorbed by wool changes abruptly between

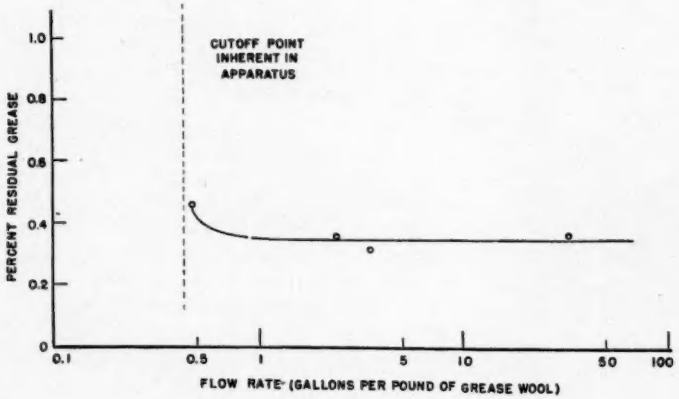

FIG. 22. *The effect of flow rate ratio of solution to wool on the residual grease.*

ethyl and propyl alcohols, while amyl alcohol is not adsorbed to any significant extent. This is attributed to the difference in molecular size of the alcohols in relation to the size of the capillary spaces in wool. The adsorbed alcohol is stable to heating at 100°C, but it is readily displaced by water [24].

In a 3% solution of butyl alcohol the wool fiber is probably sufficiently swollen by the water to permit adsorption of butyl alcohol. In order to determine whether butyl alcohol is selectively adsorbed by wool from an aqueous solution, a clean, scoured sample of wool was immersed in a 3% solution (solution-to-wool ratio, 10:1) for 24 hrs. at 60°C. The concentration of butyl alcohol in solution before and after immersion was determined refractometrically with a dipping refractometer. No change in concentration was detectable by this method of analysis.

During the course of scouring, as more and more wool is fed through the system, the suint concentration in the recirculation scouring solution gradually rises. The effect of this increasing suint concentration on the efficiency of removal of grease is shown in Figure 23. The data were obtained at a constant flow rate at 60°C in a 3% butyl alcohol solution.

Although the results indicate that the residual-grease content of the scoured wool is relatively independent of suint concentration, it was observed that the gradual build-up of suint causes a distinct discoloration of the scoured wool at the higher concentrations (above 3%, approximately). This discoloration is believed to be due to an organic pigment, lanuarin [23]. Since the color of the scoured product is of as great importance as the residual-grease content, this factor will determine the level to which the suint concentration can rise before partial removal is necessary.

The final disposition of the suint wastes from the process has not been completely explored. Obviously, the simplest solution is to recover the butyl alcohol and discharge the remainder into the sewer if local regulations permit. Since the effluent is highly concentrated and is relatively free of grease and dirt, it should be readily amenable to biological treatment by municipal sewage-treatment plants. Another factor of interest is that the suint liquor, as a result of the bactericidal properties of butyl alcohol, does not putrefy even on prolonged exposure. This is in rather marked contrast to the usual wool-scouring waste, in which putrefaction occurs almost immediately and gives rise to extremely objectionable odors.

An alternative suint-disposal method is recovery by evaporation. This procedure at first appears attractive since the suint solution is relatively concentrated and is free of dirt and grease. Unfortunately, there is no potential market for suint, except as a possible source of potash or fertilizer; hence, its recovery seems rather impractical. There is a genuine need for more knowledge concerning the chemical composition of suint, which might lead to economical utilization of this large-volume waste.

In the clarification of the scouring waste by an increase in alcohol concentration, the major difficulty encountered is that of recovery of a pure grease from the precipitated sludge. The grease and dirt tend to coprecipitate from solution to form a strongly bonded complex.

As a first approach to this problem, an attempt was made to selectively extract the grease from the

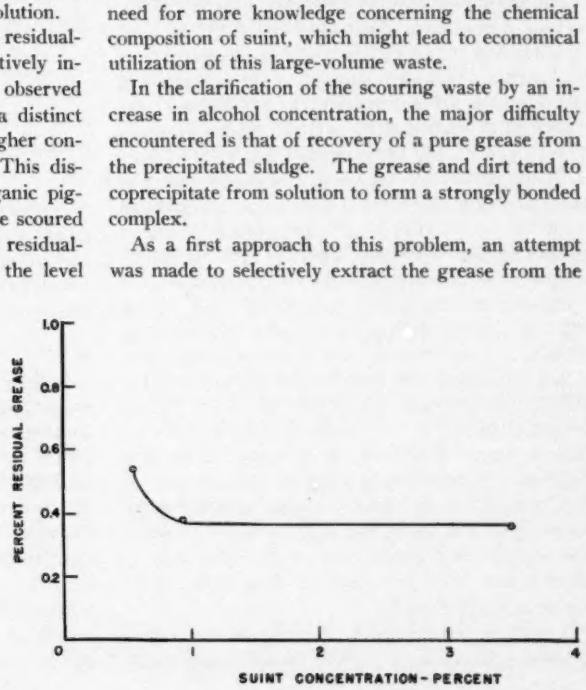

FIG. 23. *The effect of suint build-up on residual grease.*

sludge by introducing a second water-saturated butyl alcohol phase. In practice this is a rather simple procedure, for it merely involves the addition of sufficient butyl alcohol to form a two-phase liquid system. The lighter butyl-alcohol-rich phase floats on the surface. The sludge, which is intermediate in density between the two liquid phases, floats at the interface, thus facilitating the extraction of the grease into the top butyl alcohol layer. This top layer is subsequently siphoned off, the grease recovered by distillation, and the butyl alcohol recycled.

If the extraction is carried out at an elevated temperature (50° to 60° C) with adequate mixing, the grease is soluble to the extent of 10%. However, since the water-saturated butyl alcohol is a rather poor grease solvent and since the grease is strongly bonded to the dirt and surrounded by a protective shell of water, the rate of extraction is slow and incomplete. Even under the best conditions, less than 50% of the total grease available can be recovered from the floating sludge. Attempts to improve the efficiency of the extraction by the addition of various additives have thus far proved unsuccessful.

An alternative method of grease recovery is the use of conventional plate-and-frame filter presses. This method has proved successful in the recovery of grease from the sludge obtained by the acid-cracking and from the calcium hypochlorite processes for the treatment of wool-scouring wastes. Grease recovery as high as 75% has been obtained by this procedure.

In the alcohol-recovery step, the concentration of butyl alcohol in the clarified suint solution is reduced from 7% (saturated) to 3% by removal of excess alcohol in the overhead vapors. This is readily accomplished because, although butyl alcohol boils at a higher temperature than does water (117.71°C at 760 mm.), the volatility of the alcohol in an aqueous solution is much greater than is that of water—that is, the vapor given off from such a solution is richer in butyl alcohol than is the solution itself. If recovery of alcohol is carried out by means of a continuous, simple distillation, as illustrated in the flow diagram (Figure 21), a material balance relating feed composition to vapor composition and bottom composition will show that it is necessary to distill over approximately one-tenth of the total feed in order to accomplish the necessary separation and recovery of butyl alcohol.

It has been established by investigation of several different types of wool that the process is applicable to wools of high or low grease content and high or low suint content. In the case of the wool which was low in suint content, it was necessary to start the scouring with suint accumulated from previous runs. Unless a suitable sequestering agent is employed, pulled wools cannot be scoured successfully by the process because of the presence of calcium from the depilatory operation.

In conclusion, although these carefully controlled laboratory experiments are of limited value in determining the technical feasibility of the process, certain inherent advantages are evident:

1. Scouring is effected under neutral conditions, insuring a minimum of damage to the fiber.
2. Effluent clarification and grease recovery are part of the process.
3. The alcohol is relatively nontoxic, relatively noninflammable, readily available, and easily recoverable by distillation.
4. The suint can be recycled as fresh scouring solution in a continuous operation.
5. The presence of the alcohol inhibits putrefaction of the scouring solution, thus making possible the reuse of the scouring solution over an extended period.
6. The process appears adaptable to existing scouring equipment.
7. The process operates within a relatively narrow concentration range and is, therefore, potentially more economical than are conventional solvent methods which require complete distillation in each cycle.

It may be of interest to mention the possible adaptation of the basic principles discussed in this report to processes other than raw-wool scouring—*e.g.*, commercial-laundry practice, oil recovery from seed meal, etc.

Summary

A study of the influence of the lower homologs of primary, aliphatic alcohols in aqueous solution on the scouring of raw wool by the natural suint salts is reported. As the chain length of the alcohol is increased, progressively less added alcohol is required for effective grease removal. A maximum effect of alcohol concentration is reached, beyond which added alcohol tends to break the grease emulsion and correspondingly less grease is extracted. For the completely water-miscible alcohols at higher concentrations, the grease is removed by the solvent action of the alcohol. That the lower concentrations of alcohol in-

fluence scouring by synergistic interaction with suint is illustrated by the ineffectiveness of alcohols in these concentrations when raw wool is previously desuinted by steeping in warm water. Consideration of the thermodynamic aspects of the process shows that at low concentrations added alcohols influence grease removal by phase partition. The correlation is in agreement with Traube's rule.

These experimental results have provided the basis for the demonstration, on a limited laboratory scale, of a continuous alcohol-suint scouring process for raw wool, under neutral conditions, with the simultaneous recovery of grease. *n*-Butyl alcohol has been intensively studied because its properties seem particularly suited to the process. A 3% solution is optimum for scouring. Further addition of alcohol to about 7% concentration, saturating the water, causes the scouring emulsion to break and the grease and dirt to separate. The alcohol concentration is then readjusted by distillation and the solution used again for scouring.

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Degradation of Cellulose During Mechanical Processing

Part II: Action of Beaters on Cotton*

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Abstract

Previous work [9] on the degradation of cotton during mechanical processing has been extended to include a study of the action of the pickers under various operating conditions. The results indicate that blade and carding beater types cause different amounts of degradation, that the amount of degradation caused by a very close setting can be differentiated from that due to wider spacings, and that the speed of rotation of the beater has a degradation effect which is detectable only after several passes—*i.e.*, several consecutive picker operations. The effect of consecutive picker operations under similar conditions of the other variables is readily discernible.

IN A RECENT INVESTIGATION [9] it was suggested that cotton degrades during the normal processing operations which convert the seed cotton to yarn. Evidence of this degradation was based upon the progressive reduction in D.P. of a given cotton as it was mechanically processed, the viscosity of cotton in cupriethylene diamine being used as an index of D.P. Hess *et al.* [6] and Forziati *et al.* [5] have also reported reduction of D.P. of cellulose during purely mechanical treatment, although the results in both of these cases were obtained on much more drastic treatments. All three of the reports cited concluded that mechanical energy could be absorbed by the cellulose and utilized to break valence bonds.

In the light of these conclusions, it seemed desirable to extend the experimental work, concentrating on the damage incurred in a single operation, with specific study of controllable variables in the operation. In the work presented here, special attention was given to the action of the beaters in the picking operation, since previous evidence showed [9] that this operation was the most drastic in causing degradation. The Saco-Lowell Shops processed the cotton to provide information on the effects of beater type, speed (r.p.m.), setting, and repetition of passes through beating equipment.

It has been argued that the damage during mechanical processing is not important with respect to that which occurs during later chemical processes such as kier-boiling or bleaching. However, a recent paper which reported studies on rain-grown and irrigated cottons [10] does not support this argument. Observed D.P. differences on samples from two stages of mechanical processing indicated degradation but were not large enough to be statistically significant (probably due to sensitivity of the method employed, which was entirely adequate for the purposes intended). However, after these samples of card sliver and combed yarns had been given identical scouring treatments, significant differences existed. Thus, although the data are not extensive, there is strong statistical evidence to indicate that the small changes in D.P. incurred during mechanical processing persisted and were not lost in the subsequent chemical treatments. An appreciable portion of the difference in D.P. of the two raw cottons also persisted through the mechanical and chemical treatments. Further experimental work in this field is intended.

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It has also been argued that lack of inclusion of studies of the D.P. of wastes in the original work [9] invalidates the conclusions, on the basis that high molecular weight materials might have been concentrated in the wastes. However, it is known that immature fibers are concentrated in the picker wastes, and the work of Hessler, Merola, and Berkley [7] indicates the molecular weight of the cellulose in immature fibers to be about half that of mature fibers obtained from the same source. Thus, the wastes should contain a predominant amount of the low molecular weight cellulose from the original sample, and exclusion of this material would tend to raise the D.P. of the samples from material at successive stages of the process; this change is the opposite of that experimentally determined. The objection is consequently unsound and invalidates neither the previous nor the present conclusions.

No comparison of the Krieble [9] and A.S.T.M. methods [1, 4] has previously been reported, because of restrictions on sample concentration by the A.S.T.M. method which are not imposed by the other method. Extensive comparison cannot be effected with the data here presented. However, where possible, comparisons have been made at constant concentration and the results are presented in Appendix B (page 562). Further work is under way in which comparison of the two methods is the primary object.

As in the previous paper, the intrinsic viscosity, $[\eta]$, will be used as an index of the molecular weight. Although a specific linear relation between D.P. and $[\eta]$ is frequently written, it is probably better to consider that a definite, but less specific relation exists. Thus, the values of the intrinsic viscosities will serve as an *index* of the D.P. rather than as a direct measure. This concept, which would mean that a 20% decrease in $[\eta]$ shows a definite degradation of the cotton, but not necessarily in the exact amount of 20% of the original molecular weight, would be consistent with viscosity-molecular-weight studies.

Methods and Samples

Industrial Experiment

The cotton was a bale of $1\frac{1}{32}$-in. Middling cotton, grown in the central belt, presumably Arkansas; according to U.S.D.A. tests, this cotton had the following properties:

Upper quartile length	1.12 in.
Mean length	0.94 in.
(coefficient of variation = 28%)	
Fineness	4.8 μg./in.
Maturity	82%
Pressley Index	7.30
(average of 6 tests)	

Processing was conducted by the Saco-Lowell Shops on standard equipment in which blade and carding beater blades could be interchanged, the speed of rotation of the blades could be adjusted to 530 or 1040 r.p.m., and the settings could be varied from $\frac{3}{32}$ in. to $\frac{8}{8}$ in.

The cotton bale was first opened and then sliced parallel to the long dimension into twelve sections. These slices were laid upon the floor, sampled, and blended by taking small portions randomly from the various slices and running them through a standard vertical opener. The mixed and opened cotton was divided into eight fractions. Each fraction was fed to one operation on one beater in which speed and setting were maintained constant. Each fraction was divided into eight sub-fractions designated A through H. The sub-fractions were used for recycle operations, the position of the letter designation in the alphabet indicating the number of passes through the beater (*i.e.*, letter A designates one pass; letter H designates eight passes).

Samples which were set aside for tests were taken in small amounts from the finished lap at various times during any one treatment and finally combined into samples of approximately 2 lbs. each. Duplicate samples were stored in the Saco-Lowell Shops; the processed cotton, in the form of laps, was also stored there.

The flow sheet shown in Figure 1 indicates the experimental design. It will be recognized as a simple factorial pattern in which three of the variables—type, speed, and setting—are investigated at two levels each (*i.e.*, two specific values of the variable, as 530 and 1040 r.p.m., and blade- and carding-type beaters), while the last variable—number of consecutive passes—is investigated at each of eight levels (*i.e.*, passes). It is apparent that the number of samples, exclusive of those obtainable from the bale and vertical opener, is $2^3 \times 8$, or 64. Obviously, some selection from this extensive list is necessary in an exploratory experiment. It was decided that the initial experiments should be 16 in number ,exclusive of bale samples,

or 2^4. The first and eighth passes were selected for test of the effect of repetition of process.

From Figure 1, it will also be seen that one inconsistency exists in the factorial pattern. While settings originally selected were $\frac{3}{32}$ in. and $\frac{5}{8}$ in., as minimum and maximum obtainable, it was found, after conducting the experiments with the carding beater at these settings, that $\frac{3}{16}$ in. was the minimum obtainable with the blade beater. This change in close setting between the two beaters makes the factorial design partially incomplete, a problem which will be discussed at greater length later.

Laboratory Experiment

Samples, as received, were stored in a conditioned room at 70° ± 1°F and 65% ± ½% R.H. When any sub-sample was removed from one of the main sample bags for solution in cupriethylene diamine, other sub-samples were analyzed for moisture content. Sub-samples were homogenized by hand-mixing and weighed in the same conditioned room on a balance sensitive to 0.1 mg. Those for moisture analysis were placed directly in weighing bottles and analysis conducted as previously described [12]. Those for viscosity measurement were weighed directly into the solution tubes, 15 ml. of solvent was added, and the contents of the tubes mixed in a thermostat under an atmosphere of nitrogen; 10 ml. of the solution was transferred to the viscometer, also in a thermostat, and times of flow measured under different applied stresses. Values of the viscosity-counterpart, ζ, were calculated and, subsequently, values of the intrinsic viscosity were obtained from the relationship of $\log \zeta_{sp}/C$ *vs.* concentration, following the method of Krieble [9].

Selection of order of running various sub-sample concentrations was by random numbers.

Results and Discussion

For each sample, the best straight line, on $\log \zeta_{sp}/C$ *vs.* C coordinates, was determined by the method of least squares.* Because of the techniques of measurement of quantities of cotton and solvent, it seemed reasonable to assume that concentration could be measured without error, so that the method of least squares was applicable. An estimate was made of the variance of the points from each best line and the various sample lines were compared to see whether they could be considered to be parallel. This test gave no evidence that the hypothesis of parallelism should be discarded. Therefore, all final values of $[\eta]$ were calculated using the mean of each line and the common slope. As a matter of interest, this slope, whose value is 7.342 (with 95% confidence limits of 7.157 to 7.527), agrees remarkably well with the composite slope of 7.268 from Empire samples, as reported by Krieble.

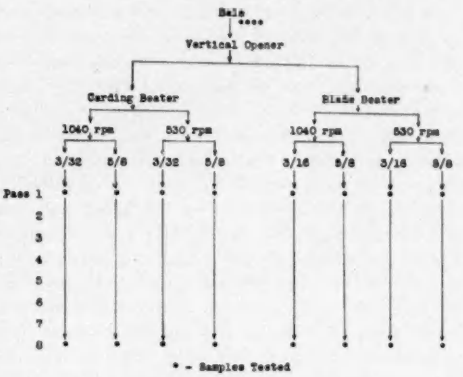

FIG. 1. *Cotton picker experiment flow sheet; factorial design.*

The calculated values of $[\eta]$ are shown in Table I, in the factorial form, together with the value for the bale. Four of the twelve bale slices were studied; comparison of the data for the individual slices gave no evidence indicating a probability of distinguishing between these individuals; they have therefore been considered as a single sample throughout, with approximately four times the number of points on this line as on those for the other samples.

Figure 2 illustrates the comparative degradation indices, calculated for each sample as a percent of the bale value. Although drawn to show most specifically the effect of increased number of passes, which is quite obvious and quite consistent, certain other effects are evident. The carding beater appears to degrade the cotton more than the blade beater, and there is some evidence that the degradation is more severe at high speed than at low, and at close setting than at wide. Decision as to significance of these last three effects requires a more exact analysis.

Obtaining complete information from the data is impossible without resort to the analysis of variance

* For standard statistical methods, reference to Brownlee [2], Cochran and Cox [3], or Snedecor [11] is suggested.

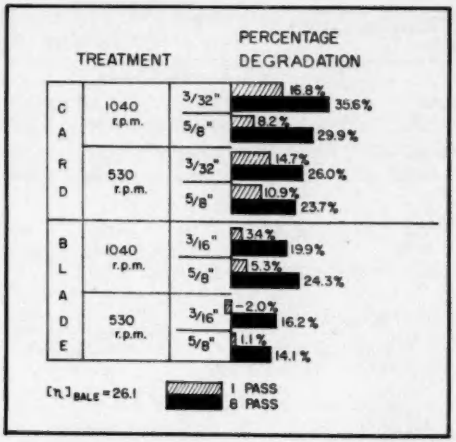

FIG. 2. *Degradation indices as a function of type of operation. Degradation expressed as percent of intrinsic viscosity of bale sample lost in each type of processing.*

for which the experiment was designed. The best form for analysis is that shown in Table III, where passes and speeds are combined into a new comprehensive factor, designated B, and beater type and settings are similarly combined into a single new factor, A.

Analysis of variance for this arrangement of the data is presented in Table III. Detailed discussion of the analysis of the various terms will be found in the Appendix, along with other statistical procedures. At this point it need only be stated that the following conclusions may be decisively drawn after completing the analysis of variance on the Saco-Lowell experiment:

1. An increase in the degradation of the cotton accompanies increasing numbers of cycles through the beater.

2. The carding beater causes greater degradation than does the blade beater under similar conditions of speed and setting.

3. An interaction exists between speed of rotation and number of passes, due apparently to a lack of ability to differentiate the contribution of different speeds of rotation until more than one pass has been completed.

4. A setting of $\frac{3}{32}$ in. has a much more drastically degrading action than one of $\frac{5}{8}$ in. when the carding beater is used, with no similar test available with the blade beater.

5. Differentiation of effects of settings was impossible above a minimum spacing of $\frac{3}{16}$ in.

Future Work

Work on deterioration of cotton from all kinds of processing, both mechanical and chemical, will be continued. Particular attention to the ginning, kier-boiling, bleaching, and finishing processes is intended.

Appendix A

Statistical Analysis of Data

Uniformity of Bale Samples

The results of analysis of variance on the four bale samples are presented below. Since consideration of all four as a single sample does not significantly increase the estimated variance from regression over that pertaining to the individual samples, it was concluded that all four could be considered as a separate single sample.

Source	Sum of squares	d.f.	Mean square
Deviations from single line	0.215252	24	
Deviations from 4 individual least squares lines	0.199341	18	0.011074
Difference	0.015911	6	0.002652
	${}_6F_{18} < 1.00$		

Homogeneity of Variance Estimates from Regression

Data pertinent to the calculations in this and the next sections are summarized in Table II. The first test applied to these data was Bartlett's [2] for homogeneity of the individual estimates of variances from the least squares regression lines. The calculation of χ^2 is as follows:

$$\chi^2 = [\sum_r (n_r - 2)] \ln s_p^2 - \sum_r [(n_r - 2)(\ln s_r^2)]$$

$$= 154.5453 - 146.0899 = 8.4554,$$

where $\sum_r$ = summation over the r lines ($r = 17$); s_p^2 = pooled value of all estimates of variances from individual regression lines; s_r^2 = estimate of variance from rth regression line; n_r = number of experimental points on the rth line. The calculated value of $\chi^2 = 8.46$ is on 15 degrees of freedom and consequently represents less variation among observed mean squares than would occur on the average when the variance was truly constant. It should be noted, however, that the pooled values of mean squares for all single-pass samples, for all eight-pass samples, and for the bale are 22.8, 46.4, and 89.7 on 32, 37, and 24 degrees of freedom,

TABLE I. SUMMARY OF [η]; FACTORIAL DESIGN
(BALE = 26.1)

	Carding beater				Blade beater			
	1040 r.p.m.		530 r.p.m.		1040 r.p.m.		530 r.p.m.	
	3/32 in.	5/8 in.	3/32 in.	5/8 in.	3/16 in.	5/8 in.	3/16 in.	5/8 in.
1 Pass								
Code No.	1A	2A	4A	3A	8A	7A	5A	6A
Intrinsic viscosity	21.70	23.95	22.25	23.26	25.19	24.69	26.78	25.81
8 Pass								
Code No.	1H	2H	4H	3H	8H	7H	5H	6H
Intrinsic viscosity	16.81	18.29	19.31	19.91	20.87	19.76	21.85	22.40

TABLE II. REGRESSION FROM LEAST SQUARES LINES

Sample No. (Code)	n_r	[η]*	Original least squares $s_{y\cdot x}^2 \times 10^4$	Original least squares $\log (s_{y\cdot x}^2 \times 10^4)$	Parallel lines $s_{y\cdot x}^2 \times 10^4$
1A	6	21.70	11.631	1.0656	13.167
1H	3	16.81	0.261	—	—
2A	5	23.95	21.058	1.3234	22.568
2H	6	18.29	27.121	1.4333	40.635
3A	5	23.26	11.168	1.0479	11.410
3H	8	19.91	64.067	1.8067	64.861
4A	5	22.25	9.300	0.9685	9.442
4H	7	19.31	82.535	1.9167	117.205
5A	5	26.78	18.858	1.2758	30.310
5H	7	21.85	40.941	1.6121	46.006
6A	7	25.81	31.732	1.5014	53.656
6H	6	22.40	22.040	1.3432	22.541
7A	7	24.69	20.342	1.3083	24.569
7H	7	19.76	42.953	1.6330	49.436
8A	8	25.19	40.202	1.6042	51.617
8H	8	20.87	41.234	1.6152	53.962
Bale	26	25.74	89.688	1.9527	90.960
Total	126		49.377		
	123 (ex. 1H)		49.916 (91 d.f.)	1.6983	47.93 (106 d.f.)

$$\sum_r [(n_r - 2)(\ln s_r^2)] = 146.0899$$

$$[\sum_r (n_r - 2)] \ln s_p^2 = 154.5453$$

$$\chi^2 = 8.4554 \text{ (15 d.f.)}$$

* For parallel lines.

respectively. This evidence of dependence of variance on sample history may be worthy of investigation at a later date; it is not of sufficient magnitude to affect subsequent calculation.

Parallelism of Lines for Separate Samples

The procedure for test of parallelism is as follows.*

* This test may be conducted in the manner used by Krieble [9] or it may be more along the lines used in study of the uniformity of the four bale samples. Since the tests are identical, the results will also be identical. The method presented was chosen solely because of the desire to have estimates of the variances of the individual lines drawn with a common slope, if use of such a common slope appeared to be justified.

The least squares common slope of all lines, with a value of

$$\sum_r \sum_i x_{ri} y_{ri} / \sum_r \sum_i x_{ri}^2 = 7.3418 = k, \qquad (1)$$

is first determined. The double summation, $\sum_r \sum_i$, indicates a summation of points on the rth line and a further summation of these sums for all lines. The use of x and y indicates deviations of values of C from their mean and of $\log \zeta_{sp}/C$ from their mean, respectively. Next, the sum of squares of deviations of the points for each sample from the least squares line with common slope is calculated. If

k is used to indicate the value of the common slope as determined from equation (1), this sum of squares may be written

$$d_{y\cdot x}^2 = k^2\sum_i x_i^2 + \sum_i y_i^2 - 2k\sum_i x_i y_i, \qquad (2)$$

the notation being as previously described. Finally, the sum of all the values is obtained from equation (2) for all lines, and the analysis of variance follows:

Source	Sum of squares	d.f.	Mean square
Deviations from least squares lines through common slope	0.508108	106	0.004793
Deviations from individual least squares lines	0.454238	91	0.004992
Difference by imposing condition of parallelism	0.053870	15	0.003591
	${}_{15}F_{91} < 1.00$		

It is apparent that no distinction can be made between the individual least squares lines and the least squares lines which have the additional restriction of being drawn parallel.

In this analysis, the data for the 1H sample were not included because only 3 points were available. Inclusion of these data could not have affected the conclusions drawn.

Fiducial Limits of Slope

The standard deviation of the slope was calculated by the usual equation [11],

$$s_k = \sqrt{\frac{s_{y\cdot x}^2}{\sum_r \sum_i x_{ri}^2}} = 0.09263.$$

With the large number of degrees of freedom, 90, involved in the pooled value of $s_{y\cdot x}^2$, t at the 5% level may be taken equal to 2.0.

Confidence limits of the slope at this level will, therefore, be

$$7.342 \pm 2(0.093) = 7.156 \text{ to } 7.528.$$

It has been noted earlier that Krieble's value [9] for the Empire cotton sample, 7.268, was well within this range.

Analysis of Variance of Main Experiment

The simplest arrangement of the data is shown at the top of Table III. Here the symbols A and B are used to indicate combinations of beater types and settings, and combinations of speed and number of passes, respectively. Because of the difference between the close settings on the two beaters, it is not possible to separate these effects completely. The analysis of variance at the bottom of the table therefore contains this combination effect. Conclusions may be drawn from this analysis, but would be simpler from one dealing with two classifications only, A and B, as follows:

Source	d.f.	Sum of squares	Mean square
A	3	33.96	11.32**
B	3	82.40	27.47**
AB	9	2.67	0.30

** Significant at 1% level.

It is thus clearly evident that combinations of speed with number of passes, and combinations of settings with beater type, are both significant effects. This information would be inadequate in itself but may be amplified by a method of comparing individual means, as suggested by Tukey [13].

According to this method, the smallest value of a difference between adjacent means which is large enough to be significant is based upon a t-test with error estimated by the AB mean square of 0.30 on 9 d.f. The least significant difference (L.S.D.) is estimated as follows:

$$\text{L.S.D. } (5\%) = t_{.05}\sqrt{\frac{2(0.30)}{4}}; \quad t_{.05} = 2.26 \text{ (9 d.f.)}$$

$$= 0.87, \text{ for means of 4 items.}$$

To apply the test, the means are arranged in numerical order and differences between adjacent values examined to see where the L.S.D. of 0.87 may be exceeded. Two sets of data from this experiment may be examined in this manner—that for the A combinations and that for the B combinations:

A *Combinations*

Source	Sums of 4	Means of 4	Differences
B ($\frac{1}{16}$)	94.69	23.67	
B ($\frac{1}{8}$)	92.66	23.16	0.51
C ($\frac{1}{8}$)	85.41	21.35	1.81**
C ($\frac{1}{32}$)	80.07	20.02	1.33**

(B = blade beater; C = carding beater.)

B *Combinations*

Source	Sums of 4	Means of 4	Differences
530 (1)	98.10	24.52	
1040 (1)	95.53	23.88	0.64
530 (8)	83.47	20.87	3.01**
1040 (8)	75.73	18.93	1.94**

(530 and 1040 = r.p.m.; 1 and 8 = passes.)

** Significant at 1% level (L.S.D. = 1.25).

A *Combinations.*—The carding beater degrades the cotton more than the blade beater since both

TABLE III. COMBINATION OF TYPE AND SETTING

Data

	Passes	r.p.m.	A† C ($\frac{3}{32}$)	C ($\frac{1}{8}$)	B ($\frac{3}{16}$)	B ($\frac{5}{8}$)	Totals
	1	1040	21.70	23.95	25.19	24.69	95.53
	1	530	22.25	23.26	26.78	25.81	98.10
B	8	1040	16.81	18.29	20.87	19.76	75.73
	8	530	19.31	19.91	21.85	22.40	83.47
		Totals	80.07	85.41	94.69	92.66	

Analysis of Variance

Source†	d.f.	S.S.	M.S.		Probability
A = T, S, TS	3	33.96	11.32		**
N	1	6.64	6.64		15%
P	1	74.09	74.09		7%
NP	1	1.67	1.67		*
NA = NT, NS, NTS	3	1.07	0.36		
PA = PT, PS, PTS	3	0.31	0.10	0.30	
NPA = NPT, NPS, NPTS	3	1.29	0.43	(9 d.f.)	
	15				

† *A* = combination of *T* and *S*. *T* = beater type, *S* = beater setting, *N* = beater speed (r.p.m.), *P* = number of passes.
* Significant at 5% level.
** Significant at 1% level.

values of the card type are significantly below those for the blade. Settings of $\frac{5}{8}$ in. and $\frac{3}{32}$ in. are also distinguished, but those at $\frac{3}{16}$ in. and $\frac{5}{8}$ in. are not. Although these latter effects are not free of the possibility of interaction, it would appear that severe degradation at extreme minimum settings is readily reduced by a small increment in spacing and that further increase will effect no further appreciable change in the cellulose.

B *Combinations.*—There is excellent evidence for the conclusion that eight passes effect more degradation than does a single pass, regardless of beater speed. However, 530 and 1040 r.p.m. are differentiated clearly only at the larger number of passes. The *PN* interaction in Table III is thus clarified. Effects of speed changes are not apparent until accumulation of degradation has been amplified by multiple passes. These same conclusions could have been drawn from Table III and a second split analysis [1] where single-pass and eight-pass data were analyzed separately.

The mean decreases in $[\eta]$ from the bale value are as follows:

1040 (1)	2.22
530 (1)	1.58
1040 (8)	7.17
530 (8)	5.23

It is interesting to note that the two values at the lower speed, 1.58 and 5.23, are 71% and 73% of the comparable high speed values. Therefore, the effects of speed are not entirely additive.

Individual Values of $[\eta]$

In Table I and Figure 2, it will be seen that the value of $[\eta]$ for the blade beater, at 530 r.p.m., $\frac{3}{16}$ in., and one pass, is greater than the estimated bale value. This situation, for a reasonably mild treatment, is not surprising. With an estimated error variance of 0.30 on 9 d.f., an individual value of $[\eta]$ may be expected, on 95% confidence limits, to be within $\pm(2.26)\sqrt{0.30} = \pm 1.24$ of the measured value. Therefore, a single value of $[\eta]$ would have to be greater than 27.3 before the fact of its excess above the bale value becomes significant. The value cited from the table was only 26.8; its size is not cause for unusual alarm.

Appendix B

Data for all 1040 r.p.m. runs on both beaters have been recalculated by the A.S.T.M. method [1]. According to that standard, a fluidity is calculated for a cotton sample dissolved in cupriethylene diamine solvent in a concentration of 0.5 g. of dry cotton per 100 ml. of solvent. In order to allow for the effects of variable rate of shear in these non-Newtonian solutions, the fluidity, *F*, is normally calculated at a velocity gradient, *G*, of 500 reciprocal

TABLE IV. COMPARISON OF A.S.T.M. AND AUTHORS' METHODS

Pairs	Sample Code	Sample Conc.	A.S.T.M. F @$G=100$	A.S.T.M. F @$G=500$	η_{sp}/C from F F_{100}	η_{sp}/C from F F_{500}	Δ F_{100}	Δ F_{500}	Authors' η_{sp}/C	Δ
1	1A	0.1013	11.9	14.8	58.5	44.8	+ 0.9	+ 6.0	130.9	+ 9
	2H	0.1088	11.3	15.7	57.6	38.8			121.8	
2	1A	0.2627	2.8	4.4	106.8	67.1	+ 2.5	+ 8.4	1990.0	+504
	2H	0.2506	3.0	5.2	104.3	58.7			1486.0	
3	2A	0.1429	6.2	9.7	85.9	52.1	+16.5	+ 7.1	298.2	+119
	1H	0.1409	7.6	11.3	69.4	45.0			178.7	
4	2A	0.1145	9.2	13.1	69.4	46.0	+10.9	+ 5.5	157.2	+ 55
	1H	0.1104	11.0	15.0	58.5	45.5			102.4	
5	B	0.0642	15.4	17.5	67.6	57.4	+24.3	+23.0	86.0	+ 20
	7H	0.0695	20.5	23.8	43.3	34.4			65.9	
6	B	0.2067	3.9	5.7	96.4	64.7	+14.5	+ 7.6	1082.7	+322
	7H	0.2131	4.5	6.2	81.9	57.1			760.0	
7	7A	0.0904	9.6	12.9	83.5	59.5	− 2.2	+ 3.9	103.1	− 13
	8H	0.0965	8.9	12.5	85.7	55.6			115.7	
8	2A	0.1429	6.2	9.7	85.9	52.1	+ 9.8	+ 4.3	298.2	+ 48
	8H	0.1439	6.9	10.5	76.1	47.8			249.5	

seconds. Since the data in this experiment were not obtained at this or any fixed concentration, comparison at fixed concentration can only be obtained with a few pairs of samples. The results of calculations on these pairs are reported in Table IV. All variables except number of passes have been disregarded in formulating this table; one of the samples in each pair has received a single beating or none; the other has had eight passes.

The following points are worthy of note although the data are too scanty to be conclusive. The differences in values of η_{sp}/C are, on the average, greater when fluidity is calculated at a velocity gradient of 100, rather than 500, reciprocal seconds. The differences in η_{sp}/C are much smaller when this quantity is obtained by the A.S.T.M. method than when it is obtained by the method of Krieble. For these data, however, there is qualitative agreement between the results calculated by the A.S.T.M. method and that of the authors.

Further experiments are under way to effect better comparisons of these methods.

Symbols

In Analysis of Variance Tables

A—combinations of T and S: T, S, and TS
B—combinations of P and N: P, N, and PN
F—Snedecor ratio (subscripts designate d.f.)
N—speed of rotation, r.p.m.
P—number of passes
S—setting
T—type of beater
PN—interaction of P and N
TS—interaction of T and S

General

C—concentration of cotton in cupriethylene diamine
d.f.—degrees of freedom
F—fluidity (subscripts designate value of velocity gradient)
G—velocity gradient
k—common slope of parallel lines
L.S.D.—least significant difference [13]
M.S.—mean square
n_r—number of points on rth line
S.S.—sum of squares
s_k—standard deviation of slope
ζ_{sp}/C—reduced intrinsic viscosity counterpart [8]
$[\eta]$—intrinsic viscosity
χ^2—chi-square [2]

Acknowledgment

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Correction

In the article "The Oxidation of Cellulose by Chromium Trioxide—A New Method for Determining Accessibility," by Ronald E. Glegg, which appeared in the March, 1951, issue of TEXTILE RESEARCH JOURNAL, it was stated that "acetic acid and acetic anhydride were purified by boiling under reflux with chromium trioxide, followed by distillation *in vacuo*." The acetic anhydride-chromium trioxide mixture is explosive, and the procedure noted is therefore incorrect. The acetic anhydride was purified by fractional distillation alone. Only the acetic acid was purified by refluxing with chromium trioxide followed by distillation.

The Influence of Weathering and of Microorganisms on the Aqueous-Extract pH of Cotton Fiber*

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Abstract

Exposure of cotton in the field to wet weather following normal opening of the boll and fluffing of the fiber resulted in increases in the pH of aqueous extracts of the fiber, as determined by methods herein described, from a level in the general range of pH 6.3 to 7.3 for the unweathered fiber to progressively higher values. The maximum pH attained was in the range of 9.5 to 10.0, and was sometimes reached within a period of 5 days.

Cotton fiber subjected to wet weather during the process of boll opening, with the consequent unfluffed and darkened appearance characteristic of "fungus tight-lock" and "boll rot," had pH values ranging from 5.3 to 9.7. In the case of the common *Diplodia* tight-lock, serious fiber weakening and fiber disintegration were accompanied by pH values from 5.6 to 6.8.

Pure-culture laboratory tests involving inoculation with fungi and humid-atmosphere incubation of fiber and unbleached cotton fabric, followed by pH determinations, indicated that several microorganisms, including certain types of common occurrence on field-weathered cotton, may bring about very rapid pH increases of the same general magnitude as those observed with fiber exposed to humid weather in the field. Both cellulose-decomposing and noncellulose-decomposing fungi brought about pH changes, which were upward in direction for 24 of the 27 isolates tested. Once high pH values were attained, no subsequent decrease in pH occurred during incubation periods of 4 weeks' duration. On water-saturated cotton fiber mats, certain common bacteria and a common yeast produced pH increases. Data suggest that increases in the aqueous-extract pH of cotton fiber may be caused by the decomposition of malic or other organic acids in the fiber by microorganisms.

Fiber which had attained a high aqueous-extract pH during weathering exhibited a decline in this value with time in storage. In tests here reported, the higher the original pH of the sample, the more rapid was the initial rate of decline in pH during storage. A decline in pH may occur also while the fiber is still on the plant in the field.

The pH test appears to offer promise as a rapid method of fairly wide applicability for detecting the growth of microorganisms on cotton fiber. The pH change measured is a response to growth on the noncellulosic constituents of the fiber and must be supplemented by further tests if one is to determine whether or not structural damage to the fiber has occurred.

General Background

When a mature cotton boll opens, the normal sequence of events is for the fiber to dry and fluff out within a period of a few hours, usually not more than 24 hours being required. If, however, high humidity or rain prevail in the period after the boll has started to open and before the fiber has dried, microorganisms may grow upon and severely damage the undried fiber. Instead of fluffing out in the normal manner, the fiber remains in a compact mass, which often turns dark in color as a result of microbial growth. The degree of injury to the fiber depends on the length of the period during which it remains in a moist condition. Damage may be so severe that the weakness of the fiber is readily apparent when it is broken in the hands, while microbial growth and obvious fiber injury are evident by simply mounting the fiber in water and examining it under the microscope.

The symptom complex described above has been termed "fungus tight-lock" and has been discussed in some detail in a previous paper [9]. Factors which

* Paper presented at a meeting of The Fiber Society, Atlanta, Georgia, April, 1951.

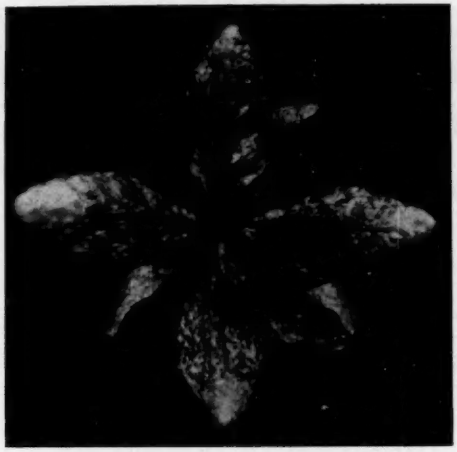

FIG. 1. *Boll infected with* Diplodia gossypina *and exhibiting the dark, unfluffed fiber typical of* Diplodia *tight-lock. The fiber is weakened and shows evident disintegration under the microscope. In the past, numerous intergrading conditions between that pictured here and that shown in Figure 2 have all been called by the loose term "boll rot." If the boll opens sufficiently to enable the cotton to be picked, the present authors class the condition as "tight lock" rather than "boll rot."*

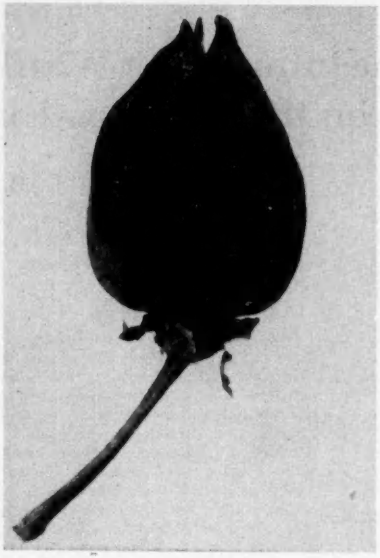

FIG. 2. *Boll infected with* Diplodia gossypina *and exhibiting the typical appearance of the true* Diplodia *boll-rot. The boll never opens and the fiber inside is destroyed.*

influence the leafiness of the plant and the degree of leaf-shading of the bolls are important in determining the incidence of fungus tight-lock. The level of moisture supply to the plant, fertilizer practices, the adequacy of insect control, inherent differences in the natural tendency of the plant to shed its leaves at the time of boll maturity, and several other factors are included in this category. Chemical defoliation offers considerable promise as a preventive measure.

A typical example of fungus tight-lock, caused in this case by *Diplodia gossypina,* is shown in Figure 1. Numerous intergrading conditions occur between this type of appearance and that of the true *Diplodia* boll-rot, shown in Figure 2. Tight-lock symptoms in the advanced stages are usually conspicuous in the field. Nevertheless, after ginning and mixing, tight-lock fiber may be difficult or even impossible to detect in a sample of predominantly undamaged fiber.

Cotton which has dried and fluffed normally may still develop fungus growth on the fiber during subsequent damp or rainy weather. The microorganisms usually present are *Alternaria, Cladosporium, Fusarium,* and certain yeasts and bacteria, the first four of which have been discussed and pictured in a previous article [7]. Growth of this sort may eventually produce the typical "blue stain," which is severely penalized in the grading of cotton. In the periods of a few days or weeks of intermittently rainy weather which so commonly occur before harvest, it is still not clear to the authors just how serious are the effects of microbial growth of this type on other use-value fiber properties. All present indications from their observations lend support to the belief that in so far as strength and length are concerned, the effects are much less severe than in the case of fungus tight-lock and are probably in many cases quite unimportant in any practical sense.

Sunlight is well recognized as an important cause of strength losses in cotton fabrics exposed for prolonged periods, especially in thin, open-weave fabrics. With cotton in the boll and with normal harvesting practices, however, such preliminary evidence as is now available suggests that individual fibers are rarely as seriously damaged by sunlight as is commonly the case with fungus tight-lock.

Earlier Contributions on pH Effects

In 1945, Fargher reported that after samples of unbleached cotton fabric had been exposed to a humid atmosphere for a few days, aqueous extracts from the cloth exhibited a much higher pH than was found with extracts from unexposed samples [4, 5]. He suggested the possibility that this result might have been due to the metabolic decomposition of salts of unspecified organic acids in the fiber by microorganisms. At about the same time, the occurrence of malic acid in relatively large amounts in the cotton fiber was demonstrated [11].

In 1948, McCall, Cirino, Stark, and Guthrie [10] published limited data showing increases in the aqueous-extract pH of cotton fiber following exposure to rainy weather. These authors mentioned the possibility that growth of microorganisms might have played some part in the pH change observed, but were inclined to regard leaching of organic acids out of the fiber by rain as the more important if not the sole causal factor.

Elting [2] has recently reported that tests for both pH and water-soluble reducing-substance content of the fiber have been found useful for the detection of microbially infected fiber. The sensitive nature of these tests is recognized by Elting, and the probability that many samples showing pH and reducing-substance values characteristic of infected fibers may not be damaged from the standpoint of use value (personal communication).

The work reported in the present paper was undertaken to determine the conditions under which aqueous-extract pH changes may occur with cotton fibers and to obtain information on the direction, magnitude, and speed of such changes, the causal factors and mechanisms involved, and the role which microorganisms might play in the process. Information on certain phases of the subject matter is still incomplete, and the present contribution is therefore in the nature of a progress report on a line of investigation to which further attention is currently being devoted.

Methods

All of the aqueous-extract pH results on cotton fiber reported in this paper were obtained by a single standard method, with the exception of a very few cases in which specific mention to the contrary is made in the text. This standard method may be described as follows:

Distilled water for the extraction was boiled for several minutes in a 2-l. Erlenmeyer flask, which was then connected to a gas-washing tower containing a dilute NaOH solution in order to prevent the absorption of CO_2 by the water as it cooled. A rubber stopper was placed on the flask after the water had cooled, and was removed as little as possible during the period of use of water from the flask. 15.0 cc. of this water, having a pH between 6.0 and 7.0, was added to 1.00 g. of fiber in a 50-cc. Pyrex weighing bottle, the fiber kneaded in the water for about 30 sec. with a glass rod, and the pH of the liquid determined on a Beckman glass-electrode pH meter equipped with a 5-cc. cup. After a high pH determination, it was necessary to rinse the electrode carefully with water and with the new test solution in order to obtain a reliable reading. Approximate checks on the figures obtained with the glass electrode were obtained by adding a small amount of Gramercy Universal pH indicator solution to a separate 5-cc. portion of the extract and examining it by transmitted light in a test tube of about 13-mm. outside diameter. Samples varying in size from 100 mg. to 10.0 g. are easily tested by simple modifications of the above method.

The choice of the 15:1 liquid-to-fiber ratio used in the tests here reported was based primarily on convenience rather than on any theoretical considerations. Using this ratio with a 1-g. sample and with the 5-cc. cup of the pH meter, sufficient extract is available for the washing of the electrode, which is required to obtain accurate values. Ratios of 9:1, 15:1, 21:1, and 27:1 have, however, been tried with a few samples. When 1-g. samples of unweathered cotton and of weathered cotton of medium and high pH were tested at these four water-to-fiber ratios, the values obtained, in the order of increasing ratio, were 6.69, 6.67, 6.82, and 6.80 for the unweathered sample; 7.46, 7.49, 7.42, and 7.35 for the medium-pH weathered sample; and 9.36, 9.24, 9.12, and 8.98 for the high-pH weathered sample. It is obvious that small errors in the water-to-fiber ratio are not of critical importance in their effect on the pH values obtained.

The pure-culture tests on cotton fiber and fabric exposed over water were carried out by the simple method illustrated in Figure 3. Fiber samples of 1-g. dry weight were placed on glass beads over water in 500-cc. bottles with screw-top caps, were steam-sterilized at about 15-lbs. steam pressure for

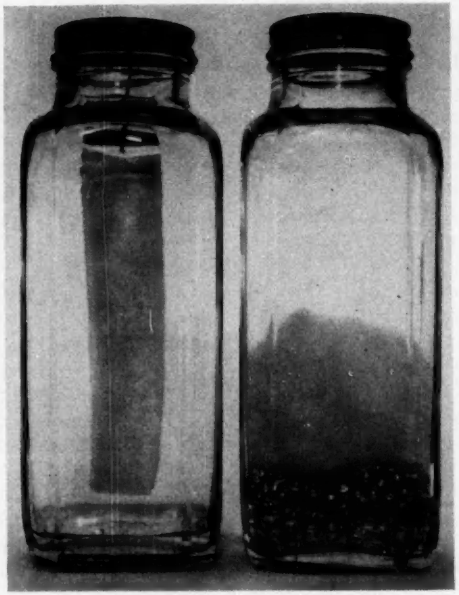

FIG. 3. *Culture bottles prepared for use in experiments of the type of Table III with fabric and fiber. In the experiments of Table IV, glass rods were used to support the fiber rather than glass beads.*

15 min., and were then inoculated by dusting under pure-culture conditions with the spores of certain fungi. The dry spores were applied with a sterile camel's hair brush. Incubation was carried out at approximately 30° C. Fabric was treated in the same way as the fiber except that it was suspended from a nichrome wire hook inserted into the liner of the bottle cap. In the experiments of Table IV, glass rods were used to support the fiber rather than beads, the rods having been found to be more convenient to handle. The shaking-culture tests of Table VI were carried out in the usual fashion on a reciprocal-motion shaking machine which made 90 complete cycles per minute.

The fungus cultures used were isolates to which reference has been made in an earlier publication [8], with the exception of the *Nigrospora* isolate, which was obtained from cotton of the 1950 crop at Stoneville, Miss. The bacterial isolates used were obtained from Mr. N. R. Smith and the isolate numbers used are his numbers. They are common, aerobic spore-forming types, discussed in a monograph by Smith and coworkers [14]; they are usually considered to be soil inhabitants, but have been isolated from a wide variey of substrata, including cotton fabrics [13]; they are noncellulolytic [13].

Results of Field Experiments

Table I presents the results of experiments which were carried out on individual-boll samples from cotton plants at the Pee Dee Experiment Station, Florence, S. C., and at the Delta Branch Experiment Station, Stoneville, Miss., in the fall of 1950. Determinations of pH were made on aqueous extracts from the fiber of bolls tagged on the day of opening with small tags labeled to identify them as bolls which had opened on that date. *No bolls affected with fungus tight-lock were included.* Some of the bolls were collected for pH test on the day of opening, and others on each of several succeeding days. The first four taggings were made at Florence, and the fifth at Stoneville.

The first tagging was made on August 22. These bolls were subjected to a cloudburst on the 23rd and to another on the 25th. After a total of 4 days of exposure, the pH values had risen from approximately 7 to over 9. At the end of an additional 13 days of exposure, the pH was in the range of 9.8.

A second tagging was made on August 27, and bolls were collected 2 days later and 4 days later. The weather during this 4-day period included a light rain on the 29th and another on the 30th, but no cloudbursts such as occurred in the first 4 days of exposure of the bolls of the first tagging. In general, the pH increases which occurred during the 4 days of weathering of fiber of the second tagging were less than those occurring with the bolls of the first tagging in a similar time period; one boll in the second tagging showed a pH of 9.5 on the 4th day and another gave a value of 9.6, while the remainder yielded lower values.

On September 4, a third tagging of opening bolls was made. The fiber of these bolls was subjected to rain on each of the first 5 days of the exposure period, an unusually severe sequence of wet weather. After a total of 5 days, the pH had risen to approximately 9.8. A slight grayish cast began to be detectable on the fiber in these bolls at about this time. Tests on fiber of bolls collected after 6, 7, and 14 days of weathering indicated that a distinct leveling-off in pH occured at a maximum in the range of 9.8 to 10.0.

TABLE I. RESULTS OF DETERMINATIONS OF pH ON AQUEOUS EXTRACTS OF FIBER FROM INDIVIDUAL BOLLS TAGGED ON THE DAY OF OPENING AND WEATHERED IN THE FIELD *

Date of boll opening	Days of weathering	pH of aqueous extracts of fiber from individual bolls	Notes on precipitation
8/22/50	0	7.0, 7.1	Cloudburst of 1.60 in. beginning at 6:30 P.M. on 8/23, and another of 0.93 in. from 5:30–6:30 P.M. on 8/25
8/22/50	4	9.3, 9.5, 9.6, 9.1, 9.3, 9.7, 9.1, 9.6	
8/22/50	17	10.0, 9.9, 9.8, 9.7, 9.7, 9.9	
8/27/50	0	6.9, 7.1, 7.5, 7.2, 7.4, 7.3, 7.3, 7.5	Light rain of .08 in. on afternoon of 8/29, and another of .15 in. on morning of 8/30
8/27/50	2	8.6, 8.5, 8.3, 9.1, 7.6, 9.1, 8.2, 7.6	
8/27/50	4	8.8, 8.6, 7.3, 8.9, 9.5, 7.6, 7.4, 9.6	
9/4/50	0	7.4, 7.3, 7.1, 7.3, 7.1, 7.2, 7.4, 7.0	Rain of .40 in. on morning of 9/5, with .25, .75, .50, and .60 in. on the next succeeding 4 days
9/4/50	2	7.7, 7.8, 7.5, 7.8, 7.4, 8.0, 7.2, 7.4	
9/4/50	3	8.0, 7.6, 9.2, 8.5, 9.4, 8.6, 8.2, 7.8	
9/4/50	4	8.5, 7.6, 9.7, 9.0, 9.7, 9.3, 8.6, 8.4	
9/4/50	5	9.7, 9.7, 10.0, 9.5, 10.0, 9.6, 9.9, 9.9	
9/4/50	6	9.7, 9.8, 9.8, 9.9, 8.8, 8.0, 9.5, 9.8	
9/4/50	7†	9.9, 8.4, 9.6, 9.9, 9.3, 9.5, 9.9, 9.5	
9/4/50	14	9.8, 8.4, 9.6, 10.1, 9.8, 9.9, 10.0, 9.9	
9/12/50	0	6.9, 6.8, 7.0, 6.9, 6.8, 6.9, 6.8, 7.1	No rain during total exposure period; heavy dew each night which remained on fiber till 9–10 A.M. (dew almost every night in all exposures at Florence)
9/12/50	2	7.3, 7.2, 7.2, 7.3, 7.2, 7.2, 7.3, 7.3	
9/12/50	3	6.8, 7.2, 7.1, 7.3, 6.6, 6.7, 7.0, 6.9	
9/12/50	6	7.3, 6.9, 7.1, 7.0, 7.2, 6.9, 7.1, 7.2	
9/12/50	7	7.2, 7.2, 7.1, 7.3, 7.3, 6.9, 7.2, 6.9	
9/12/50	8	6.8, 7.0, 7.6, 7.1, 7.1, 7.0, 7.3, 7.1	
9/12/50	9	7.3, 7.1, 7.3, 7.2, 7.4, 7.4, 6.7, 7.5	
10/12/50	0	6.8, 6.6, 6.9, 7.0, 6.8, 7.0, 6.6, 6.8	Rain of .27 in. on 10/19, .15 in. on 10/21, and 1.2 in. on 11/1 (20th day of exposure)
10/12/50	2	6.5, 6.9, 6.4, 6.4, 6.6, 6.8, 6.9, 7.0	
10/12/50	4	6.4, 6.8, 6.6, 6.7, 6.5, 6.3, 6.2, 6.8	
10/12/50	5	6.6, 6.8, 6.6, 6.5, 6.7, 6.4, 6.2, 6.8	
10/12/50	6	6.5, 6.7, 6.6, 6.8, 6.6, 6.8, 6.7, 6.4	
10/12/50	7	6.7, 6.5, 6.6, 6.7, 6.6, 6.8, 6.6, 6.3	
10/12/50	8	6.5, 6.3, 6.6, 6.6, 6.7, 6.4, 6.5, 6.7	
10/12/50	11	6.8, 6.7, 6.6, 6.5, 6.7, 6.8, 6.4, 6.5	
10/12/50	12	6.6, 6.5, 6.8, 6.7, 6.3, 6.8, 6.7, 6.6	
10/12/50	20	7.3, 7.4, 7.2, 7.6, 7.9, 7.6, 7.4, 7.3	

* Exposures beginning on 10/12/50 were at Stoneville, Miss.; all others were at Florence, S. C.

† The high pH values noted for cotton fiber exposed to damp weather on the station grounds at Florence were not associated with a peculiar local situation at the station, since high values were found also very commonly with the fiber of weathered bolls collected on this date on 5 farms located 2–7 miles from the station in different directions. Out of a total of 20 bolls, 4 of which were picked on each of these 5 farms, 18 yielded pH values above 9.0, and 14 were in the pH range of 9.5 to 10.2.

A fourth tagging was made at Florence on September 12. The 9-day period during which collections were made was sunny and without rain, although dew did form at night. The pH of the fiber showed a very small increase during the period of exposure.

The month of September was unusually rainy at Stoneville, Miss., in 1950. Most of the several weathered single-boll samples of unknown opening date which were collected there on September 27 showed high pH's, generally between 9.0 and 10.0. A series of newly opened bolls tagged on October 12, however, was favored by relatively dry weather until the 20th day of exposure and did not show a rise in pH until that time.

It was apparent from the data of Table I that the development of high pH was correlated with the occurrence of wet weather. In both the Florence and Stoneville areas both high-pH and low-pH cottons were picked in commercial practice in 1950, the pH being dependent on the weather between the time of boll opening and picking. Due to differences in the time of opening of bolls on a single plant, mixtures of high-pH and low-pH cotton were undoubtedly common. It also seemed probable from the data of Table I that the maximum pH attained by cotton fiber in the field was in the range of pH 9.5 to 10.0. This latter conclusion was further supported by observations on cotton in

TABLE II. AQUEOUS-EXTRACT pH VALUES FOR COTTON SUBJECTED TO PROLONGED WEATHERING ON THE PLANTS IN 1950–51
(SAMPLES ANALYZED WITHIN 2–3 WEEKS AFTER COLLECTION)

Location of growth	Approx. date of picking	pH of aqueous extracts from individual bolls	No. of bolls with organisms present in medium to large amounts				
			Alternaria	*Cladosporium*	*Fusarium*	Yeasts	Bacteria
Auburn, Ala.	Feb. 15	7.2, 9.7, 8.5, 7.2, 10.0, 7.6, 8.6, 9.3	7	7	6	2	8
Marianna, Ark.	Feb. 15	8.1, 7.3, 7.8, 6.6, 6.8, 7.7, 7.6, 7.9	8	7	0	2	8
Stoneville, Miss.	Feb. 15	7.6, 6.9, 7.9, 8.1, 7.8, 9.1, 7.9, 7.9	8	8	4	0	8
Holly Springs, Miss.	Feb. 15	8.8, 8.9, 9.0, 8.9, 8.3, 8.7, 8.7, 8.8	8	8	1	1	8
Florence, S. C.	Mar. 7	8.3, 7.7, 7.3, 8.1, 6.8, 7.9, 7.0, 7.8	8	8	2	2	5

the field at Stoneville, Miss. Bolls which had already undergone weathering were tagged at this station on September 29 and harvested at weekly intervals for a period of 8 weeks. The original pH on September 29 was in the range of 9.6–9.8 and the values remained consistently in the range of 9.0–9.8 for the entire period. Under some circumstances, however, fiber pH may decline again during prolonged field weathering. Cotton which opened on September 15 at Experiment, Ga., was collected on that date and after 7, 13, 38, and 68 days of weathering, during which time the total cumulative rainfall for weathered collections amounted to .03, .15, 2.6, and 3.7 in., respectively. All of the rain between the 13-day and 38-day collections fell in a period of 5 days preceding the latter collection. The pH values increased rapidly during this period of 5 days to a level of 9.4–9.9, but showed a decline at the 68-day collection date, with values ranging from 7.7 to 9.9. Samples from the 68-day collection were classed as Strict Good Ordinary.

A number of samples that had been weathered in the field for periods of from 3 to 6 months were examined to complete the picture. It is recognized that cotton that had been exposed in the field for such long periods would be below grade and of little commercial importance. These long-exposed samples had medium-to-large amounts of fungus growth and frequently low or medium pH values. Data on these points are shown in Table II. A short incubation of fiber from these bolls on water agar caused the fungi present to resume spore production. As in numerous earlier examinations of weathered cotton by the same method, *Alternaria, Cladosporium, Fusarium,* yeasts, and bacteria were found present in abundance [7]. Tests on 56 bolls other than those on which results are reported in the table were carried out on cotton picked from 7 different fields in the vicinity of Florence on March 7, 1951. The results showed an erratic distribution of pH values, ranging from 6.4 to 9.9. Several of the bolls with the darkest fiber showed lower-range pH values. Repeated extraction of high-pH cotton in the laboratory with distilled water results in a rapid decrease in the pH of successive extracts, and there seems to be no reason to believe that repeated or thorough leaching of the fiber by soaking rains would not accomplish the same result in the field, although it is also known (see page 575) that pH decreases can occur also in the absence of leaching.

In only a very few cases have cotton samples in our tests exhibited pH values below 6. A series of 8 bolls picked at Fayetteville, Ark., in February, 1951, yielded values in the range of 5.5 to 6.2. These samples had a brownish color when wet. The extracting water had a pH of 6.1.

The pH of fiber in rotton bolls and in fungus-inhabited tight-locks [9] seems to represent a special condition. Specimens of the common *Diplodia* tight-lock and *Diplodia* boll-rot collected at Florence yielded pH values generally below rather than above neutrality. Thus, 7 *Diplodia*-rotten bolls gave pH values of 5.3 to 7.5, while 9 *Diplodia* tight-locks gave pH values of 5.6 to 6.8. The several anthracnose tight-locks tested had high pH's, mostly above 9.0.

Not only the lint fibers, but also the fuzz fibers, undergo an increase in pH during humid-climate weathering, with the result that pH changes during humid weather may be detected in aqueous extracts of intact fuzzy seed. Tests were made by shaking 20 seeds with 5 cc. of water for 3 min., and then determining the pH of the extract. Unweathered seeds tested by this method yielded pH values almost identical with those of the lint fiber from the same bolls—namely, in the range 6.7 to 7.1—whereas seed from weathered bolls in which the lint fiber had increased

TABLE III. EFFECT OF INOCULATION WITH A FUNGUS AND SUBSEQUENT HUMID-ATMOSPHERE INCUBATION OF RAW COTTON FIBER AND UNBLEACHED COTTON FABRIC ON THE pH OF AQUEOUS EXTRACTS OF THE SAME*

Fungus	pH of extract from: *Fiber*, after the following number of days of incubation:					*Fabric*, after the following number of days of incubation:				
	2	3	4	7	9	2	3	4	7	9
Controls (sterile, uninoculated)	6.3	6.4	6.4	6.3	6.3	6.8	6.8	6.8	6.8	6.8
Actinomyces #98	6.8	6.8	8.6	9.5	9.7	9.0	9.2	9.7	9.9	9.9
Alternaria #122	6.8	9.3	9.6	10.0	10.2	9.2	9.8	9.8	9.9	9.9
Aspergillus flavipes 36	7.8	8.6	9.0	9.9	9.9	7.7	9.8	9.9	9.9	9.9
Aspergillus niger TC-215-4247	6.2	5.8	4.9	4.7	4.6	7.4	7.0	5.2	5.0	4.9
Aspergillus oryzae 10063	9.4	9.8	9.9	9.8	9.8	9.0	9.2	9.3	9.7	9.4
Aspergillus terreus 45	7.3	7.7	8.8	9.2	9.2	9.7	9.7	9.8	9.8	9.8
Aspergillus ustus 48.1	7.2	9.2	9.6	9.8	9.8	9.6	9.7	9.9	9.8	9.8
Aspergillus wentii 1023	8.1	8.5	9.0	9.8	10.0	8.8	9.3	9.4	9.6	9.7
Chaetomium globosum #1042.4	7.8	8.5	8.9	8.8	8.8	7.7	8.1	8.2	8.4	8.0
Circinella sydowi 9023	7.7	8.4	8.4	8.3	8.5	7.5	8.0	7.4	7.2	7.6
Cladosporium #113†	7.0	7.8	8.3	9.7	9.8	9.1	9.6	9.8	9.8	9.8
Colletotrichum gossypii #134	7.4	8.1	9.7	10.0	10.2	7.5	9.5	9.6	9.8	9.8
Cunninghamella verticillata 8985	7.2	7.8	7.8	8.5	8.7	7.4	7.5	7.5	7.2	7.5
Diplodia #135 (lock)	6.1	5.6	5.4	5.3	5.2	6.8	5.4	5.2	5.0	5.0
Diplodia #136 (burr)	6.4	6.0	5.9	5.8	5.9	7.2	6.4	6.4	5.5	6.1
Fusarium moniliforme #102	7.9	9.3	9.9	10.0	10.1	9.3	9.6	9.7	9.8	9.9
Fusarium moniliforme #1004.1	7.3	9.1	9.9	10.2	10.3	9.2	9.8	10.0	10.0	9.7
Nigrospora #137	6.7	6.8	8.5	10.0	10.0	7.2	7.8	9.0	9.7	9.3
Penicillium kapuscinskii 1336.2	8.6	8.9	9.1	9.3	9.4	8.4	8.8	8.6	8.6	8.5
Penicillium luteum #1336.1	6.6	6.9	7.4	8.2	8.2	7.0	7.3	7.5	7.5	7.5
Stachybotrys atra #35.1	6.2	6.5	7.0	8.0	9.4	7.0	7.4	7.7	8.4	9.2
Trichoderma T-1	7.2	7.9	8.0	8.6	9.0	7.8	8.0	8.2	8.7	8.8

* 1 g. of fiber or fabric ("Q" duck) inoculated by dusting with dry spores and incubated over water in a 500-cc. bottle at approximately 30°C. Pure-culture techniques were used throughout.

† Incubated at 20°C.

to a pH range of 9.0 to 10.1 yielded seed-extract pH values showing increases of from .3 to .9 pH units as compared with the extract from the unweathered seeds.

Results of Laboratory Experiments

Experiments were carried out to determine whether or not pH changes similar to those observed on fiber during humid weathering in the field could be obtained under pure-culture conditions in the laboratory. It was found that when samples of raw cotton or strips of unbleached cotton fabric were placed over water in 500-cc. bottles, steam-sterilized, and then inoculated by dusting under pure-culture conditions with spores of certain fungi comonly found on field-weathered cotton—namely, *Alternaria* sp., *Cladosporium herbarum*, and *Fusarium moniliforme* [7]—the aqueous-extract pH of the fiber rose rapidly during subsequent incubation to a level in the general range of pH 10 (Table III). Since fungi are frequently found to differ widely from one another in various aspects of their physiology, a number of fungi other than the three just mentioned were also used in similar tests in attempting to arrive at some grounds for generalizations in respect to the effect of fungus growth on the aqueous-extract pH of cotton fiber. It became apparent that major increases in pH occur with many fungi under these circumstances (Table III). Two exceptions to this type of behavior, however, may be seen in the data relating to *Aspergillus niger* and *Diplodia* sp. *Aspergillus niger* produced a distinct lowering of the pH, while two *Diplodia* isolates which produced luxuriant visible growth caused little change or a moderate decrease in pH. The action of *Aspergillus niger* in causing a decrease in fiber pH was not particularly surprising, in view of the well-known potentiality of this fungus for producing citric acid.

It may be noted in Table III that *Circinella* and *Cunninghamella* produced a much more pronounced rise in pH with fiber than with fabric. These results were confirmed for both fungi in an identical test with the same fiber and fabric, and very closely similar results were also obtained with the same fungi and two additional fiber samples and two additional fabrics. No certain explanation of this phenomenon is

at hand. It was thought at first that perhaps the two fungi did not penetrate throughout the fabric, but when ravellings of the fabric were incubated with them, the results obtained were very similar to the results with fabric. With many of the organisms of Table III, the growth was very inconspicuous at the time that the maximum pH had been attained.

Several fungi not reported in Table III have also been tested on cotton fiber and fabric under the same conditions. Tests carried out on fiber according to the method of Table III for time periods of 3, 7, and 14 days yielded maximum pH values with *Curvularia, Stemphylium, Humicola, Thielavia, Stysanus,* and *Verticillium cinnabarinum* of 10.2, 10.1, 9.3, 7.9, 10.1, and 10.2, respectively, and for fabric of 10.1, 10.0, 8.9, 9.9, 10.1, and 10.0. In view of the results obtained with the numerous genera and species tested, it seems justifiable to conclude that the property of causing increases in aqueous-extract pH of cotton is very common among the mold fungi.

The pH response during incubation of fiber at different relative humidities showed the general type of result one might have expected in the light of previously known facts about fungus growth on cotton at different humidities—namely, that rapid and considerable pH increases occurred at the higher relative humidities but not at the lower ones. Thus, when 1-g. samples of fiber were incubated at 20°C over water and over saturated solutions of 4 different salts, the results shown in Table IV were obtained. In test No. 1, the fiber was left unsterilized and uninoculated, so that the pH changes taking place resulted from the growth of unknown organisms present on the fiber. In tests Nos. 2, 3, and 4, the fiber was steam-sterilized at 15 lbs. pressure for 15 min. in bottles over saturated solutions of different salts, and was inoculated after the bottles had been held at 20°C for 3 days to insure the attainment of solubility equilibria at that temperature. The results obtained may not hold true for all isolates of the fungi tested, for all cotton samples, or for conditions deviating in various ways from those here employed.

Since bacteria occur frequently on weathered cotton fiber, a few of the more common bacteria were tested for their influence on fiber pH. The yeast *Rhodotorula aurea,* also common on weathered cotton, was likewise tested. In these experiments, 1-g. samples of cotton fiber were placed in the bottom of 500-cc. Erlenmeyer flasks, 10 cc. of water was added, and the cotton was tamped into a water-saturated mat. The flasks were then plugged with cotton plugs and sterilized in the autoclave in the usual manner. After cooling, they were inoculated, and a covering of parafilm was placed over the plugs to prevent water loss. At the end of the incubation period, 5 cc. of water was added to the saturated mat, the fiber was kneaded in the usual fashion, and pH values were taken on the extract. The maximum pH values attained during incubation periods of up to 11 days were as follows: *Bacillus brevis* 604, pH 8.0; *B. cereus* 232, pH 8.2; *B. cereus* var. *mycoides* 233, pH 8.1; *B. pumilus* 236, pH 8.4; *B. licheniformis* 1263, pH 9.2; *B. firmus* 613, pH 8.5; *B. megatherium* 234, pH 8.9; *B. sphaericus* 344, pH 8.3; *B. subtilis* 231, pH 8.1. *Rhodotorula aurea* isolates 115 and 118 attained values of pH 8.9 and pH 9.0, respectively.

There seems to be no reason to believe that changes in pH brought about by microbial growth on cotton fiber result from any action of the organism on the cellulose of the fiber. Several of the fungi listed in Table III are species which in earlier experiments were found to be unable to cause strength loss in cotton fiber—*e.g., Aspergillus oryzae, Aspergillus niger,*

TABLE IV. EFFECT OF RELATIVE HUMIDITY* ON CHANGES IN AQUEOUS-EXTRACT pH OF RAW COTTON INCUBATED IN 500-CC. CULTURE BOTTLES AT 20°C

Test No.	Inoculation	Days incubated	pH attained at relative humidities of: 100%	95%	92%	88%	84%
1	None (unsterilized)	4	9.8	7.2	6.8	6.8	6.8
		7	9.8	9.4	6.8	6.9	6.7
		14	9.9	10.0	7.4	6.8	6.9
		21	10.0	10.1	8.4	6.8	6.8
2	*Alternaria* #122	7	10.0	8.1	6.4	6.5	6.4
		14	10.2	8.2	6.4	6.4	6.3
		21	10.2	9.7	6.5	6.4	6.3
		28	10.2	9.8	6.5	6.5	6.4
3	*Cladosporium* #113	7	9.6	7.2	6.3	6.3	6.3
		14	10.0	9.7	6.5	6.3	6.3
		35	10.0	10.0	6.7	6.4	6.3
4	*Fusarium* #102	7	9.8	10.0	6.3	6.3	6.3
		14	10.0	10.1	6.8	6.3	6.3
		35	10.1	10.1	7.5	6.3	6.3

* The salt solutions used to obtain the different relative humidities and the moisture regains of the fiber as determined at these humidities were as follows: 84%, KBr, 10.9%; 88%, K_2CrO_4, 12.6%; 92%, $NaBrO_3$, 16.6%; 95%, Na_2HPO_4, 22% and higher (variable); 100%, pure H_2O, 29% and higher (variable).

Relative humidity values over the different saturated salt solutions were taken from Lange's "Handbook of Chemistry," 4th edition, Sandusky, Ohio, Handbook Publishers, Inc., 1941, p. 1234.

TABLE V. STRENGTH AND AQUEOUS-EXTRACT pH OF UNBLEACHED ("Q") DUCK BEFORE AND AFTER INOCULATION AND INCUBATION IN A HUMID ATMOSPHERE WITH *Alternaria* AND *Cladosporium**

Fungus	Days incubated	Strength (lbs.)	pH range
Alternaria #122	2	104	8.8– 9.5
Alternaria #122	3	106	9.0– 9.5
Alternaria #122	4	103	9.2– 9.6
None (control)	0	104†	6.7– 6.9
Cladosporium #113	2	103	7.7– 9.3
Cladosporium #113	3	102	9.6– 9.8
Cladosporium #113	4	103	9.6–10.0
None (control)	0	105‡	6.6– 6.9

* 10 replicate strips were used for each strength determination and 5 for each range of pH value.
† L.S.D. = 5.3 lbs.
‡ L.S.D. = 4.7 lbs.

Aspergillus wentii, Cunninghamella verticillata, and *Circinella sydowi. Diplodia* #136, on the other hand, which produced no striking change in pH, is known to be highly active in degrading cotton cellulose. Data on the above and numerous other species with respect to their ability to cause strength losses in cotton fiber are contained in a previous contribution from this laboratory [8]. When 5 in. × 1½ in. strips of unbleached cotton duck were ravelled to 1 in. in width, inoculated under pure-culture conditions with *Alternaria* and *Cladosporium,* and incubated over water in the manner of Table III, the major increases in aqueous-extract pH which occurred were not accompanied by significant losses in strength (Table V). When fiber is incubated for short time periods with pure cultures of fungi according to the method of Table III, changes in the appearance of the fiber may be seen when the Congo-red test is applied. The importance which may correctly be attached to this phenomenon, however, does not appear at all certain to the writers at the present time ([6], p. 601). It is clearly evident that the mere occurrence of a high aqueous-extract pH is not in itself sufficient to indicate that a sample of cotton has necessarily undergone significant structural degradation by microorganisms.

It is not uncommon for microorganisms to produce a pH change in one direction in their growth medium and later to cause a change in the reverse direction. Attempts to determine whether or not fungi which have produced a high-pH reaction in a cotton fiber may upon long-continued incubation bring about a reversal of the trend, with a decrease in pH, have to date shown no such action. In these experiments strips of gray duck ("Q" duck) were inoculated separately with *Alternaria, Cladosporium,* and *Fusarium,* and incubated according to the method of Table III. In order to be certain that oxygen supply might not be limiting to growth, each strip was transferred to a new sterile bottle over water at the end of each week of incubation. Each of the fungi produced pH values in the fabric in the range of 9.6 to 9.9 within the first week, with a gradual increase within the succeeding 3 weeks to a level of 10.1 to 10.2.

In comparing the rapidity of increase in pH under the pure-culture conditions of Table III with the rapidity observed in the data of Table I for field-weathered cotton, a question arises in regard to the possibility that the amount of spore inoculum used in the tests of Table III were higher than would be encountered in nature and the pH increases observed in culture unusually rapid for this reason. It must be conceded that no accurate control over the amount of inoculum used was exercised in these culture experiments and that this factor probably did influence the relative rates of increase in pH by different fungi. Evidence at hand suggests, however, that the amount of inoculum normally present on any good clean sample of cotton fiber is probably sufficient to produce rapid pH increases without any additional inoculum. It has been observed that good clean cotton fiber incubated according to the method of Table III, but without sterilization, increases in pH at a rate roughly comparable to that with many of the fungi of that table. Thus, 5 samples of Deltapine fiber grown in different locations across the cotton belt in 1948 yielded pH values under these conditions of 9.1 to 9.6 in 4 days of incubation, with further increases to values of 9.4 to 9.8 in 9 days.

Cotton linters inoculated with *Alternaria* in pure culture and incubated and tested for pH in the same manner as the fiber (Table III) yielded pH values which increased to a level of 9.4 in 4 days and to 10.0 in 11 days.

When *Alternaria, Cladosporium,* and *Fusarium moniliforme*—fungi common on field-exposed cotton —were grown in shaking culture on aqueous extracts of unweathered cotton fiber and on solutions of mineral salts containing malic or citric acids or glucose, the pH changes shown in Table VI were obtained. It may be seen from these data that ex-

tracts from raw cotton increased in pH on incubation, and that mineral-salt solutions containing malic acid did also. Glucose-mineral salt solutions, on the other hand, underwent a striking decrease in pH, while citric acid solutions did not support growth or undergo any significant change in pH. McCall and Jurgens [12] reported the presence of citric as well as malic acid in cotton fiber, although in distinctly lower amounts. It is not certain that the pH changes occurring with fiber could not be due at least in part to the decomposition of protein materials, although no volatile basic substances such as ammonia or amines could be detected by boiling aqueous extracts from high-pH cotton.

Since the shaking-culture tests of Table VI showed a decrease in pH with fungi grown on glucose and since reducing sugars occur in the cotton fiber, the question arises of why the fiber showed an increase in aqueous-extract pH as a result of fungus growth, rather than a decreased or static pH. One could imagine that the fiber pH might decrease as a result of metabolic action on sugars or that it might remain more or less constant as a result of simultaneous decomposition of both organic acids and sugars, the two reactions having a compensatory relation to each other in respect to pH. Certain possible answers may be suggested. It is believed that the fungi concerned in the shaking-culture tests of Table VI produce organic acids from glucose under these conditions, but when they are growing on the fiber under the conditions of Table III they probably produce CO_2 and H_2O instead. It may also be pertinent that sugars appear to occur in the cotton fiber

TABLE VI. pH OF AQUEOUS EXTRACTS OF COTTON FIBER AND OF MINERAL-SALTS SOLUTIONS CONTAINING MALIC OR CITRIC ACIDS OR GLUCOSE BEFORE AND AFTER INOCULATION AND INCUBATION WITH FUNGI*

	pH after incubation of:				
			Mineral-salts† solution with:		
Fungus	Cotton extract No. 1	Cotton extract No. 2	Malic acid (.583%)	Citric acid‡ (.6%)	Glucose (.5%)
None (unincubated control)	5.6	7.3	6.3	6.0	6.4
Alternaria	9.0	8.8	7.8	5.9	2.7
Cladosporium	8.9	9.1	9.1	5.9	2.4
Fusarium	9.2	9.0	9.3	5.9	3.4

* Growth for 4-day period in shaking culture; 25 cc. of solution in 125-cc. Erlenmeyer flask.

† Mineral-salt composition of medium in g./l. was as follows: NH_4NO_3, 1.0 g.; KH_2PO_4, 0.9 g.; K_2HPO_4, 0.7 g.; and $MgSO_4 \cdot 7H_2O$, 0.7 g. Vitamins B_1, B_2, and biotin were also added to the mineral salts in *Alternaria* media.

‡ No growth occurred with any of the 3 fungi on citric acid medium.

in much lower amounts than do the organic acids [12]—as indeed they do also in other parts of the cotton plant [3]—and that the pH-increase effect tends to dominate for this reason, if for none other.

The pH of cotton fiber as determined by the method described herein (page 567) does not appear to be always completely stable or constant over long time periods. On the contrary, experimental results indicate that under at least some conditions of storage of the fiber these values decrease with time.

Data on changes of pH during fiber storage were obtained with fiber from a series of 195 samples grown for spinning test purposes in 1949 at 23 different lo-

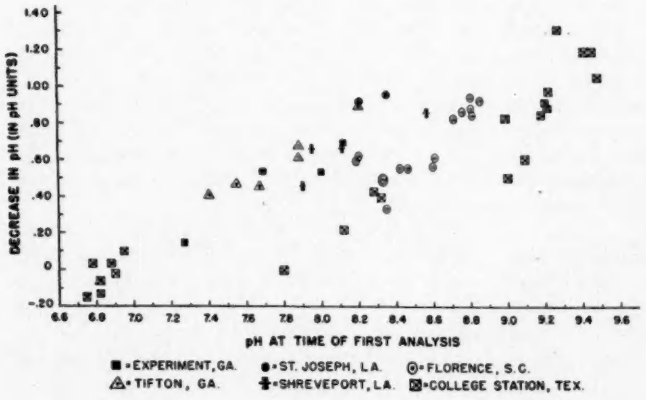

FIG. 4. *Decrease in pH of 1949 spinning test samples during storage in the laboratory for 30 weeks as related to absolute pH level. Samples were approximately 8 months old at the time of the first pH determination in late May, 1950.*

TABLE VII. AQUEOUS-EXTRACT pH OF UNWEATHERED COTTON AS COMPARED WITH THE SAME FOR COTTON EXPOSED TO WEATHERING ON THE PLANTS BEFORE HARVEST (SAMPLES ANALYZED APRIL, 1950)

Variety	Florence, S. C. 1947 crop		Florence, S. C. 1948 crop		Shafter, Calif. 1948 crop		Shafter, Calif. 1949 crop	
	Unweathered	Weathered*	Unweathered	Weathered†	Unweathered	Weathered‡	Unweathered	Weathered**
Acala 4-42	—	—	6.0	7.8	6.5	6.3	6.6	6.5
Acala 1517W	—	—	6.1	7.2	6.3	6.2	6.5	6.4
Coker Wilds	6.3	7.4	5.7	6.9	6.0	6.2	6.6	6.7
Coker 100W	6.3	7.3	6.3	7.5	6.3	6.4	6.7	6.8
Deltapine 15	6.4	7.3	5.9	6.9	6.4	6.0	6.6	6.6
Mebane (Watson's)	—	—	6.3	7.8	6.5	6.3	6.5	6.5
Rowden 41B	6.4	7.1	6.4	6.9	6.4	6.3	6.7	7.0
Stoneville 2B	6.6	7.1	6.3	7.2	6.5	6.2	6.7	7.0

* Weathered 7 weeks.
† Weathered 11 weeks.
‡ Weathered 11 weeks.
** Weathered 10 weeks.

cations scatered throughout the cotton belt from North Carolina to California [1]. All of the locations from which samples were tested in the series yielded pH averages within the range of 6.0 to 7.9, with the exception of samples from 4 locations—namely, Shreveport, La. (average pH 8.1), St. Joseph, La. (average pH 8.3), Florence, S. C. (average pH 8.5), and College Station, Tex. (average pH 8.2). At the first three of these four locations high humidities are well known to be common. The high-pH samples from College Station, Tex., were definitely darker in color than the lower-pH samples from the same location, and showed abundant microscopic evidence of fungus growth. The first pH tests on these samples were made in May, 1950, approximately 8 months after harvest. When several samples from this series were retested 30 weeks after the first test, distinct decreases in pH were found to have occurred, as may be seen from the data in Figure 4. The fiber had been stored in air-dry condition in the laboratory for the 30-week period. It will be noted from the data of Figure 4 that, in general, the higher the pH of a sample at the time of the first test, the greater was its decrease in pH during storage.

Field-exposed fiber samples which showed abundant evidence of fungus growth but which were quite old or very old at the time of testing frequently showed pH values which, on the basis of the known weathering history of the fiber, were probably lower than the maximum which had presumably been attained at one time. Thus, in Table VII the presence of moist conditions during weathering at Florence, S. C., and of dry conditions at Shafter, Calif., is reflected in the relative pH values of weathered *vs.* unweathered fiber, but the absolute level of the values generally had presumably decreased considerably since the time of harvest. In early 1950 a group of 24 dark-colored low-grade fiber samples of the crop of 1947 of several different states obtained from Miss D. Nickerson were tested for pH. As mentioned in an earlier paper [7], these samples, in general, showed a great deal of fungus growth, especially of *Fusarium moniliforme*, with *Alternaria, Actinomyces, Cladosporium,* and yeasts also being present on the fiber from several of the locations. Nevertheless, when tested for pH in 1950, all of these samples gave pH values in the range of 5.7 to 7.2.

These results suggest that it may not be uncommon for significant differences in pH among samples at the time of harvest to be lessened or possibly even to disappear during storage, with all samples tending to become not only lower but also more nearly the same in pH during storage.

Cotton samples of widely differing genetic constitution all exhibit the phenomenon of increase in aqueous-extract pH as a result of fungus growth. Among upland cotton types, for example, samples of fiber from plants of the varieties Acala 4-42, Acala 1517W, Coker Wilds, Deltapine 15, Watson's Mebane, Rowden 41B, and Stoneville 2B all yielded pH values of 9.1 to 10.0 after a 7-day saturated-atmosphere incubation with either *Alternaria* or *Fusarium*. Samples of 8 different Sea Island types gave pH values ranging from 9.1 to 9.7 after 7-day saturated-atmosphere incubation with *Alternaria* #122. A very coarse Indian cotton of the variety Garo Hill

yielded a pH value of 9.6 under the same conditions.

Cotton which has been subjected to such extreme nutritional deficiencies as to result in very low yields, very small plants, and unusually thin-walled fibers still shows the phenomenon of pH increase as a result of fungus incubation. Experimental material of this type was available at Florence, where certain fertilizer regimes have been practiced on the same land for 36 years. Fiber from the "zero fertilizer" plots yielded pH values after 7-day incubation with *Alternaria* #122 according to the method of Table III of 9.0 and 9.9, whereas fiber from the 4–8–1, 4–0–4, and 4–10–4 treatments gave pH values of 9.9, 9.8; 10.0, 9.8; and 10.0 and 10.0 under the same conditions.

In a further trial of the pH behavior of unusual cottons in humid incubation, a sample of brownish, "frosted" cotton was tested. Cotton of this type, which has opened prematurely as a result of frost, is believed to contain generally a higher content of water-soluble substances than cotton which has opened more normally. Four subsamples from one such sample (which was known to be unusually high in water-soluble substances which exert a reducing action on cupric copper and on picric acid) were incubated in a saturated atmosphere with *Alternaria* in the manner of Table III. The pH values obtained after a 7-day incubation were 9.8, 9.9, 10.0, and 10.0, very much the same as from other cottons.

Buffering substances in the liquid extracted from the fiber appear to influence the pH values obtained. Thus, when 1 g. of weathered fiber was extracted with 15 cc. of liquid of pH 6.74 obtained by previous 15:1 water extraction of unweathered fiber, a pH value of 8.38 was obtained, whereas another sample of the same weathered cotton extracted with 15 cc. of water of pH 6.2 in the usual manner yielded a pH of 9.51.

Mixtures of cotton fiber of different degrees of weathering are common in practical situations, not only on the farm, where cotton on a single plant opens at different times and encounters different weather conditions, but also in the mill, where cottons are blended. Tests were run, therefore, on the pH of mixtures of low-pH and high-pH cottons. Using a low-pH sample of pH 6.7 and a field-weathered high-pH sample of pH 9.6, it was noted that mixtures of the two containing 10%, 20%, and 50% of the high-pH fiber yielded pH values of 7.0, 7.3, and 8.4, respectively.

Boiling of an aqueous extract obtained previously in the usual manner at room temperature from a high-pH weathered cotton did not appear to drive off ammonia or any other volatile basic substance which could be detected by pH indicator paper, by odor, or by a decrease in pH of the solution. Thus, a weathered sample extracted in the usual manner at room temperature yielded a pH of 9.5, whereas the same extract after several seconds of vigorous boiling had a pH of 9.4.

High-pH fiber of either field-weathered or *Alternaria*-incubated origin undergoes a decrease in pH in a matter of a few hours at temperatures of 125°–150°C, but this is obviously rather drastic treatment, and the results hardly seem to indicate a high degree of sensitivity to dry heat. Thus, a field-weathered sample of original pH 9.5 yielded values of 9.6 and 9.4 after 6 and 24 hrs., respectively, at 100°C; of 9.4, 9.3, and 9.0 after 6, 18, and 24 hrs. at 125°C; and of 9.0, 8.7, and 8.1 after 6, 18, and 24 hrs. at 150°C. *Alternaria*-incubated fiber of original pH 10.1 gave values of 10.1, 10.0, and 10.0 after 6, 18, and 24 hrs. at 125°C; and of 9.7, 9.1, and 9.0 after 6, 18, and 24 hrs. at 150°C. Moist heat is more effective than dry heat in bringing about reduction in the pH of high-pH fiber. After 2 hours in an autoclave at approximately 121°C and 17 lbs. steam pressure, field-weathered samples of pH 9.5 and 7.7 were reduced to values of 7.3 and 6.9. The fiber samples in this experiment were placed in closed 500-cc. bottles over water and were not subjected to any leaching action from condensed steam.

Discussion

The pH test offers considerable promise as a rapid method for the detection of the growth of microorganisms on cotton. At present, however, there are certain limitations on the interpretation of the test results which must be recognized. The presence of microbial growth on the fiber does not always indicate structural fiber damage. Furthermore, the occurrence of a pH in the range of 6.3–7.3 does not always indicate the absence of growth and fiber damage. A tentative key for the interpretation of results of the pH test might be as follows:

A. Recently harvested cotton, pH 6.3–7.3

1. White or cream colored (high grade): It is fairly certain that cotton of this type has not supported

the growth of organisms and therefore could not have been damaged by microbiological action.*

2. Darkened in color (low grade): This situation occurs with cotton weathered for such long periods that the pH has risen and later declined into this range. Such fiber shows abundant microscopic evidence of fungus growth and is probably low in both strength and length.

B. Recently harvested cotton, pH above 7.3

1. Not greatly darkened in color: Cotton of this description may or may not be damaged by microorganisms. Although conspicuous on well-developed samples in the field, the dark color of fungus tight-lock may be difficult to detect when moderate amounts of tight-lock fiber are present in ginned lint. Serious microscopically visible fiber damage occurs in cotton affected with tight lock. In many cases, however, cotton which has a high pH and little or no evident darkening in color is very probably free of tight-lock fiber and is essentially or completely undamaged in respect to any use-value property.

2. Darkened in color: Cotton of this description is more likely to have suffered structural damage than that under classification *B*–1. The amount of cotton in the sample from bolls influenced with fungus tight-lock is a critical factor. The circumstances leading to fungus tight-lock have been described [9].

C. Cotton in storage

1. pH in the range 6.3–7.3: Because of the tendency for pH to drift downward in storage, pH values in this range may not be particularly informative. The longer the storage period, the less reliable is a pH in this range as an indication that growth had not occurred on the fiber at some time in its previous history.

2. pH above 7.3: Cotton in this category might exhibit a high pH because of microbial action in unduly moist storage or at some period prior to storage. Since many of the organisms which grow on and damage cotton in storage do not darken or discolor the fiber conspicuously, the pH test may be of considerable use as a preliminary test on cotton of this nature. Final proof of fiber damage would depend on evidence from supplementary tests.

McCall *et al.* [10] refer to the high pH of cotton subjected to rain in the field as probably resulting from the effect of rain in leaching organic acids out of the fiber. It is apparent from the pure-culture results of Table III that actual leaching of the fiber is not necessary in order to obtain the pH effect. It may be pointed out, however, that the moisture content of the fiber in the pure-culture tests of Table III was very high. It may be that once cotton has dried and fluffed in the field the humidity necessary to return it to a high enough moisture level to sustain rapid fungus growth and to maintain it at that level seldom occurs without actual rain. Although the close parallelism between pH results obtained in the field and in pure culture has been pointed out here, it is not claimed as proven that enzymatic or catalytic reactions of the fiber itself might not contribute to pH changes under some circumstances. Any inherent catalytic activity of the fiber is obviously inactivated by autoclaving (control samples, Table III) and it is clear that microorganisms are capable of bringing about pH changes independently of any possible additional mechanism inherent in the fiber itself.

Aqueous-extract pH values have been used by Elting [2], along with water-soluble reducing-substance content, as a means of quickly identifying microbially infected cotton fiber, and certain cotton-producing areas from which cotton of this nature was obtained have been depicted in maps [2]. Although the increased size of the areas from which such cotton was obtained in 1949 and 1950 as compared with 1948 might be interpreted to indicate a geographical expansion in the areas of occurrence of some unknown new causal agent responsible for the high pH and low reducing-substance content of the fiber, the present authors are strongly inclined to place a different interpretation on the data. The organisms which occur commonly on cotton in the field—namely, *Alternaria, Cladosporium, Fusarium,* yeasts, and the aerobic spore-forming bacteria [7]—are types which are very widely distributed and probably universally present in major or minor amounts in soils throughout the agricultural areas of the world. The anthracnose organism, *Colletotrichum gossypii,* is known to have been widespread on cotton in the southeastern part of the United States over 40 years ago [9]. A much more plausible explanation of the increased size

* *Diplodia,* which causes microscopically visible fiber damage in the tight-lock condition without an increase in pH, would almost always be accompanied by other fungi which would cause an increase in pH of the sample as a whole. If the *Diplodia* were present in major amounts there would be a noticeable darkening of the sample.

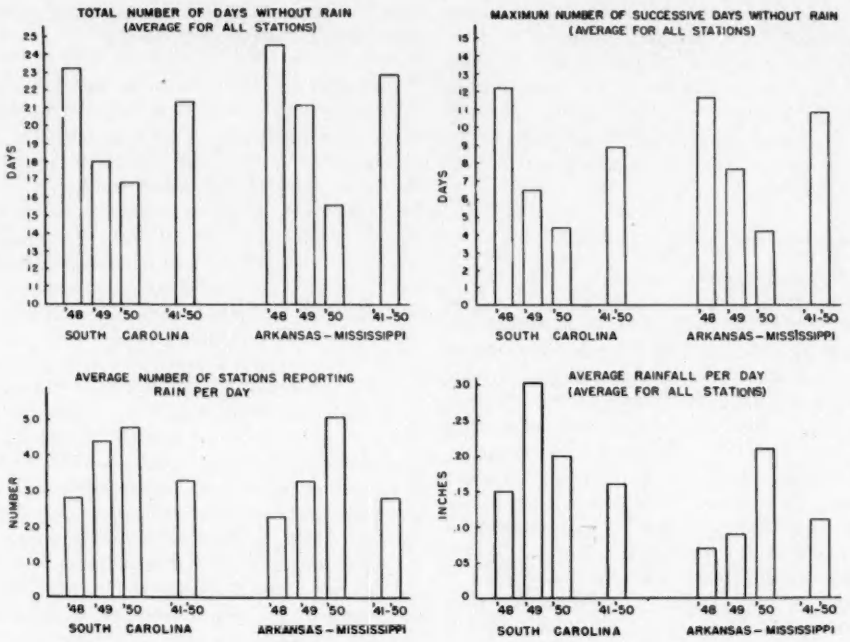

FIG. 5. *Weather data for the period August 15–September 15 inclusive, for 10 stations selected at random within each of the two major areas shown by Elting [2] as sources of microbially infected cotton in 1950. Stations in the South Carolina area included: Bishopville, Blackville, Blairs, Calhoun Falls, Clemson College, Columbia Air Port, Florence, Laurens, Spartanburg, and Wedgefield. Stations in the Arkansas-Mississippi area included: Dumas, Marianna, Parkin, Portland, and St. Charles in Arkansas; and Clarksdale, Cleveland, Greenwood, Vicksburg, and Yazoo City in Mississippi.*

of the areas from which high-pH cotton was derived in 1949 and 1950 seems to be readily apparent from the weather records at harvest time for these years. If one examines weather data for the period of August 15 to September 15 for the areas in South Carolina and Mississippi-Arkansas designated by Elting [2] as sources of infested fiber in 1950, it is seen that wet weather was much more frequent and more widely distributed throughout these areas at that time of year in 1949 and 1950 than in 1948. In studying this subject, 10 weather stations were selected at random in each of these two areas, and data compiled from these stations.

The data obtained are shown in Figure 5. The total number of days without rain in the August 15–September 15 period, on the average, for all stations is seen to have been much higher in 1948 than in either 1949 or 1950 in both areas. The 1948 total was above the 1941–50 average, while the 1949 and 1950 totals were definitely below this 10-year average in both areas.

A period of several successive days without rain is usually necessary to bring about opening of a major part of the bolls in any given field and to allow harvesting without exposure of the fiber to rain. Consequently, the number of successive days without rain would appear to be an important factor in respect to the occurrence of high-pH cotton. Figure 5 shows that the maximum number of successive days without rain during the August 15–September 15 period, calculated as an average for all stations, was much higher in 1948 than in either of the two succeeding years, as well as higher than the 10-year average.

The relative prevalence of rainfall in the years and areas concerned is also shown in Figure 5 in terms of the average number of stations (out of a total of 10

for each area) reporting rain per day during the August 15–September 15 period. Again the prevalence of rain in 1949 and 1950 as compared with 1948 is apparent.

Average rainfall per day, also shown in Figure 5, is not so reliable a criterion as the other three just mentioned for use in this connection. In 1948 a period of dry weather occurred very generally throughout South Carolina in the 17 days beginning on August 18, and much of the cotton crop was harvested before the rainy period, which started on September 4.

Acknowledgment

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INDUSTRIAL SECTION

Cavitomic Cotton*
A Progress Report

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Abstract

Damage resulting from microorganisms occurring in increasing amounts of apparently good spinnable Middling cotton and the effects on mill processing are recognized. Such cottons, called "cavitomic," are distinguished from off-color and field-damaged types. Data and observations supporting a previous publication, together with methods of observation, are given. Reducing-material content, pH, and metallic-ion content of easily soluble water extracts are discussed, and relationships between them shown. Weakening of the fiber is exhibited by shortening of staple. Data obtained under both laboratory-controlled and conventional warehouse-storage conditions are given.

Introduction

Fiber damage resulting from the action of microorganisms or their metabolic products has been observed in apparently good spinnable Middling cotton received at Kendall Mills. The alteration of fiber properties has been called "cavitoma." The present paper presents data and observations concerning these cottons and amplifies a recently published note [5]. It is a progress report covering the work done and steps being undertaken by these laboratories to appraise the significance of cavitomic cottons to Kendall Mills. Present work is being carried on in collaboration with the United States Department of Agriculture.

Deterioration of cotton under conditions of wet storage is well recognized; observations on cottons containing more than 9% moisture are reported by Fleming and Thaysen [7]. Conditions which lead to off-color and to other forms of field damage have been the subject of numerous investigations. The work of Fargher [6], in which relations of copper number and pH are discussed, is pertinent. Deterioration of weaving capacity after storage and the low quality of finished products have been associated with endoparasites by Schepkina [14]. Poor mill operation associated with high alkalinity of the cotton fiber was mentioned by Hopper [8] in the spring of 1950. More recently, the identification of microorganisms associated with forms of tight-lock and other aspects of field damage have been undertaken by Marsh [11] and Arndt [1].

All observations reported herein are restricted to Middling grades, good color, cottons ranging from 1-in. to $1\frac{1}{16}$-in. staple. The work to date shows that such cottons may exhibit measurable and significant alterations of fiber properties attributable to microorganisms or their metabolic products. The alteration of fiber properties continues during warehouse

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storage. The microorganisms or their metabolic products which are responsible for fiber damage, and conditions of growth and storage favoring cavitoma are yet to be fully established.

Increased swelling of fibers in caustic and reduction in staple length by fiber breakage are, at this stage, the most readily observable changes in fiber properties. The coexistence of high pH and a small amount of reducing material serve as rapid laboratory tests to indicate the presence of cavitoma. Other methods which give evidence of cavitoma are implied in the data which follow. Observation of fiber damage in caustic under the microscope is necessary in order to classify a cotton. Adequate methods of quickly appraising fiber damage are needed.

Early Observations

Readily determined chemical characteristics of cotton have been observed routinely in these laboratories since 1943. During this time, several instances of poor mill operation were associated with cotton having unusually small amounts of soluble reducing material. In 1947, high values of pH were also associated with poor operating conditions. Since the combination of high pH and low reducing-material content occurred in 10% or less of the cottons tested, the phenomenon was not considered to be of immediate concern.

In the fall of 1949, however, when more than 50% of the cottons submited to these laboratories were observed to have high values of pH and low contents of reducing material, the need for further investigation was apparent. In the laboratory, leaching of cotton with water had been observed to lower the amount of reducing material, but high values of pH had not been reproduced. A search for the causal agent ensued.

The high incidence of cavitomic cotton was repeated in 1950. Figure 1 shows the percentages of bales tested having various values of pH and reducing material (ESRM) * for the 3 years from 1948 through 1950. About 80 shipping points in the east and 40 in the central area are represented, the total number of bale samples varying from 1,000 to 1,500 for the years shown. The data comprise a survey of Middling grades, 1-in.–$1\frac{1}{16}$-in. staple, of interest to Kendall Mills buyers; the data, therefore, do not present an over-all crop survey. The data presented are further restricted to cottons within 8 months of ginning. Figure 2 shows areas in which cavitomic cottons were found in 1948, 1949, and 1950.

* ESRM is a symbol referring specificially to the easily soluble reducing material detected by the test method outlined.

Account of Ensuing Investigations

Publications by Marsh [10] and McCall *et al.* [12] inspired experiments to ascertain whether or not the high alkalinity might be associated with the presence of microorganisms. Counts were made of cavitomic fibers from samples of cottons having a wide range of pH and ESRM values. The data are shown in Figure 3. These observations were made by traversing the microscope field once across a hundred or more fibers arrayed on a slide, using 18% sodium hydroxide as a swelling agent. Microorganisms in or on fibers, abnormal swelling, striations, and damage to the fiber or the lumen were the criteria used. Figure 4 shows typical cavitomic fibers at moderate magnification. When more than half of the fibers were cavitomic, the pH and ESRM values were observed to be roughly constant.

Fiber damage, characteristically cavitomic, is frequently observed with few if any microorganisms apparent at moderate magnification. At higher magnification, following staining with methyl violet and swelling with 18% caustic, minute microorganisms are found within the lumen. The characteristic appearance of such fibers is shown in Figure 5.

Incubation of cottons at moderately high humidities provided means for observing progressively the increased swelling, appearance of striations, and pH and ESRM changes. Inoculation of sterile raw cotton with organisms cultured from cavitomic cotton produced similar effects.

As incubation continued, the amounts of readily water-soluble material and pectin were reduced. The benzene extractables became less and the melting point of extracted material increased slightly. No change in the amount of ionizable material was observed. The amount of reducing material decreased to a low value and remained low; at a more advanced stage it increased slightly. Bale samples classified as cavitomic exhibit similar values.

Each year since 1943 a group of 25 to 30 cottons chosen to represent a wide range of physical and chemical properties, and some varietal samples known to be aphid-infested, had been subjected to numerous quantitative tests. All tests were made within

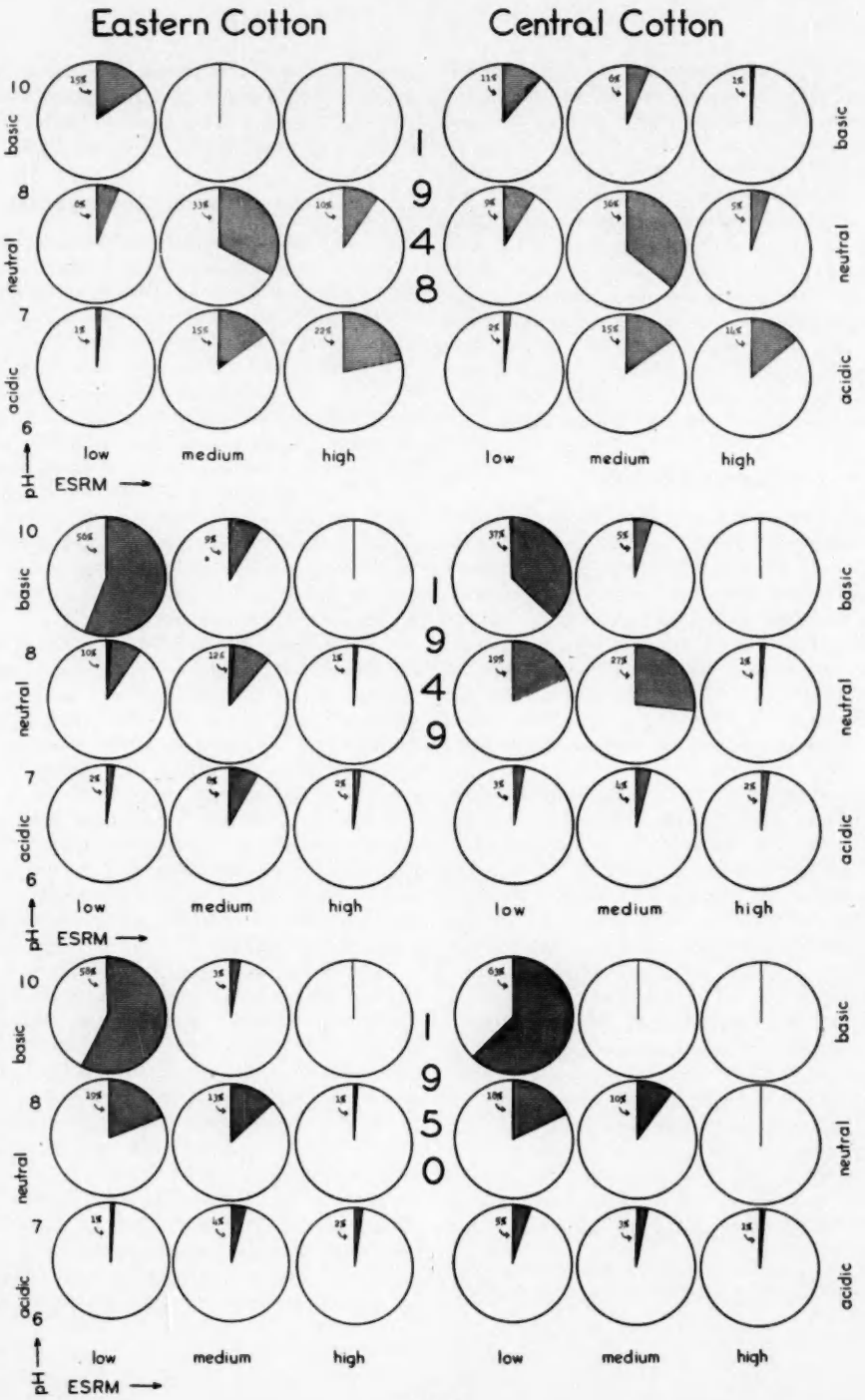

Eastern Cotton
Central Cotton
1948
1949
1950
basic
neutral
acidic
10
8
7
6
pH
low
medium
high
ESRM

FIG. 1.

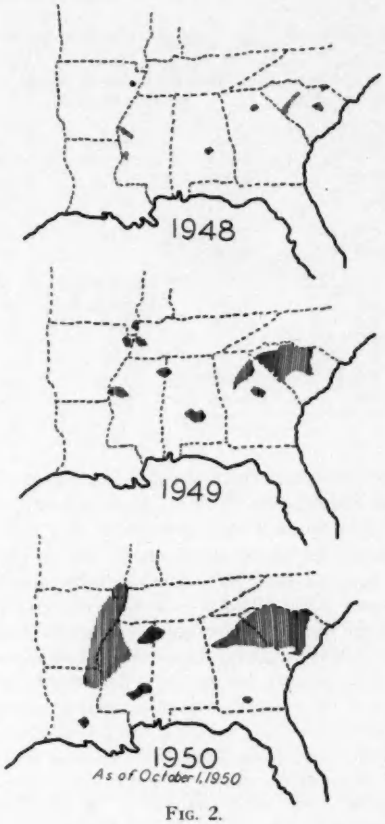


FIG. 2.

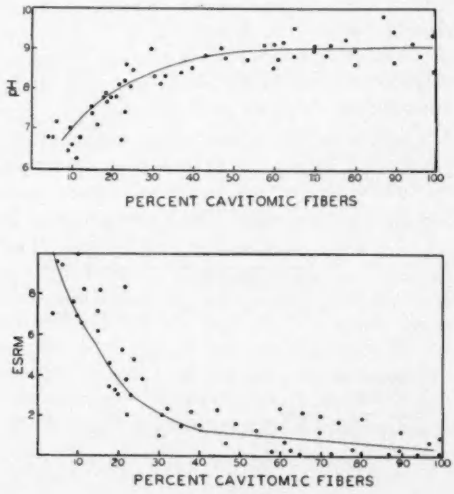


FIG. 3.

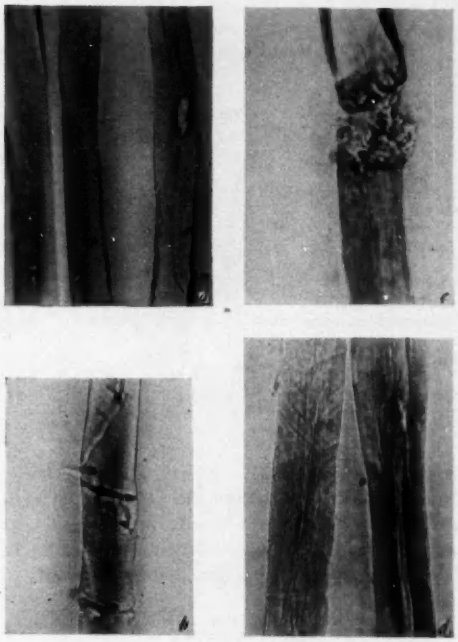


FIG. 4. *Cavitomic cotton fibers (magnification, 290 ×).* a—*Normal fibers, showing little damage.* b—*Large hyphae penetrating fiber wall (note swelling).* c—*Ruptured fiber.* d—*Striations.*

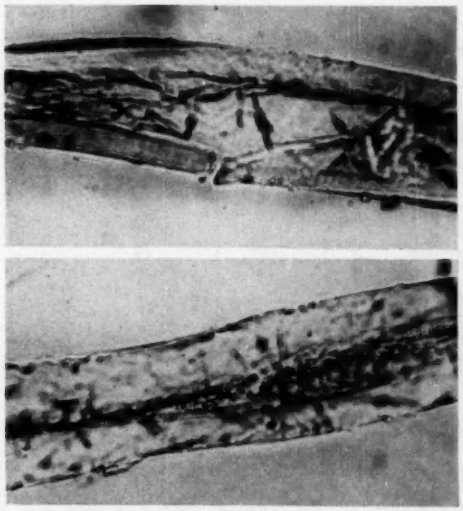


FIG. 5. *Cavitomic cotton fibers stained with methyl violet (magnification, 670 ×).* Top—*Fungus or pseudofungus in lumen of fiber.* Bottom—*Bacteria in lumen of fiber.*

TABLE I

	Tests dependent on water-soluble material					Tests dependent on water-insoluble material		
	ESRM	pH	Copper number	Ionizable matter (%)	Water-soluble matter (%)	Acid-binding capacity (Me/g.)	Benzene-extractable matter (%)	M.P.* Benzene-extractable matter (°C)
Group I								
Normal	8–10	6.0–7.0	0.8–1.2	0.8–1.0	2.5–3.0	0.065	0.65	55
Leached	6–3	7.0–7.5	0.7–0.3	0.6–0.3	2.0–1.5	0.065	0.65	55
Group II								
Early cavitoma	7–3	7.0–8.0	0.6–0.3	0.8–0.6	2.5–1.5	0.050	0.55	60
Advanced cavitoma	0–3	8.0–10	0.4–0.5	0.8–0.6	1.7–1.9	0.030	0.45	65
Group III								
Immature	8–15	6.5–6.0	0.8–2.0	0.8–1.0	3.0–5.0	0.080	0.78	50
Aphid-infested	10–15	6.0–6.5	0.8–2.0	0.8–1.0	3.0–4.0	0.065	0.65	55

* Melting point.

a few months of ginning. These data were reviewed in the light of the information derived from the incubated cottons. The steps, briefly, were as follows: Using the criteria of low ESRM values and values of pH above 8, cottons exhibiting reduced amounts of surface constituents were placed in one group. Numerous investigators [3, 9, 17] have associated high reducing value and high pectin and wax contents with immature fibers. High sugar content (honey dew) resulting from aphid infestation has also been recognized [16]. Using the criteria of above-average percentage of immature fibers and aphid infestation, cottons exhibiting high values of ESRM were placed in another group. Among the cottons which fell in neither of the above two groups, several possessed low values of ESRM and ionizable material and yet exhibited none of the other characteristics of cavitoma. Incubated cottons, however, had shown no change in the ionizable material. The amounts of reducing and ionizable materials were thus seen to provide a means of discriminating between the three groups of cotton. The data are plotted in Figure 6.

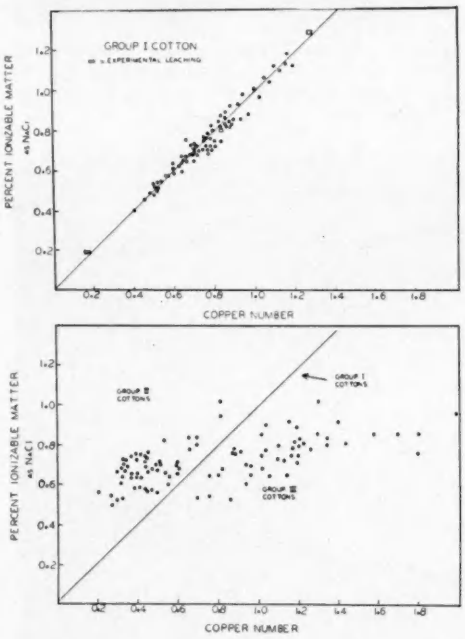


FIG. 6.

The cottons that were not classified as cavitomic, immature, or aphid-infested were found to fall along a straight line, as shown in Figure 6 (top). The points plotted as open squares were experimentally water-leached cottons. By elimination, therefore, these cottons are "normal." The cavitomic cottons fall to the left of the normal line, shown as Group II

TABLE II

	% Cavitomic fibers		
Sample no.	1	2	3
Uncombed fibers	50	30	60
Combed fibers	20	20	20
Waste from combing	60	50	70

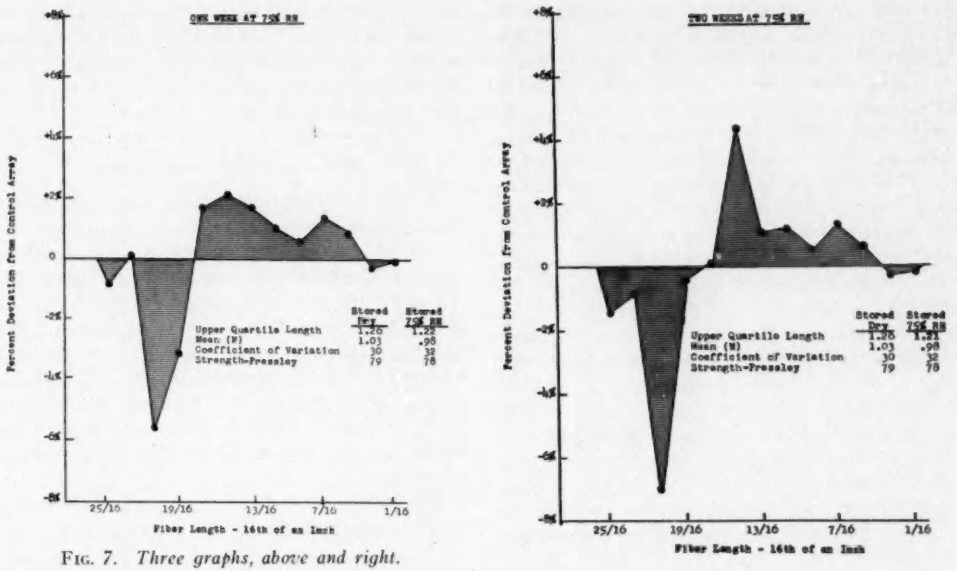


FIG. 7. *Three graphs, above and right.*

in Figure 6 (bottom); the immature and aphid-infested cottons, comprising Group III, fall to the right of the normal line. The data for these cottons are summarized in Table I.

Fiber Breakage

Cavitoma counts were made on fibers from card strips, picker laps, and card web; the averaged results of several such tests were 50%, 50%, and 30% cavitomic fibers, respectively. The counts for the picker laps and strips were approximately equal (slightly higher in strips than in laps before rounding average counts); counts in the web were lower than in either laps or strips. Observed under the microscope in caustic, the fibers from the strips exhibited generally greater swelling and damage than did the others.

In the preparation of flat fiber bundles for strength tests [2], the combing ruptures the weak or damaged fibers. Cavitoma counts were made on uncombed and combed fibers and on the waste. The data from three tests are shown in Table II. The percentage of cavitomic fibers in the uncombed cotton falls between those in the combed fibers and the waste.

The making of fiber arrays with the Zweigle or Suter-Webb sorters also involves a combing operation. Cavitomic cottons show shorter staple length with increasing time in storage. The staple decreases range from negligible, well within the prob-

able error, to about $\frac{3}{32}$ in. Arrays have been made on several cottons maintained at known conditions of temperature and humidity. The change observed in length distribution for a cotton maintained at 75% relative humidity and variable outdoor winter temperature after 1 week, 2 weeks, and 2 months is shown in Figure 7. In these graphs the original fiber array for the cotton before incubation is represented by the horizontal line at zero on the vertical axis. The decreasing percentage of long fibers and the corresponding increase of short fibers are apparent. The corresponding and more conventional fiber distributions and arrays are shown in Figure 8. In 2 months the upper quartile length of this cotton changed from 1.26 in. to 1.17 in., and the mean from 1.03 in. to 0.92 in.; the coefficient of variation changed slightly from 30% to 35%, while Pressley strengths showed no significant difference. The statistical significance of differences between arrays and the sampling errors involved in these experiments have not yet been estimated. The data are, however, adequately consistent to support the evidence.

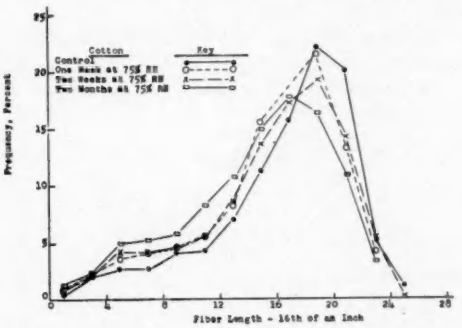
Similar results are obtained in certain warehouse-stored bales, as illustrated in Figure 9. The change in staple occurred during a 2-month period; the moisture content of this bale ranged from 7.1% to 7.6%.

Very little can be said at this stage in regard to fiber strength as indicated by conventional methods. Strength data present a decidedly wider variation than is usually associated with normally good cottons. Strength tests being made on samples drawn from bales in warehouse storage exhibit a variability so wide that it is difficult to ascribe physical meaning to averages. Several bales of non-cavitomic cotton in the same warehouses continue to yield normal strength data. Until microscopic evidence reveals that damage has become uniformly severe, consistent low strength is not found.

Miscellaneous Observations

Moisture is necessary for the growth of microorganisms, and more water is formed as nutrients are consumed. With some exceptions, microorganisms flourish at high humidity and moderate temperature; 9% moisture content is generally considered the minimum for growth in cotton. The cottons under study contain from 5.5% to 9.2% moisture, with evidence of fiber damage progressing in the 6% to 7% range. Preliminary measurements on cottons kept at fixed humidity show evidence that progressively higher moisture equilibria are attained as cavitoma increases.

The initial fiber condition, time, temperature, and moisture are undoubtedly the principal factors af-



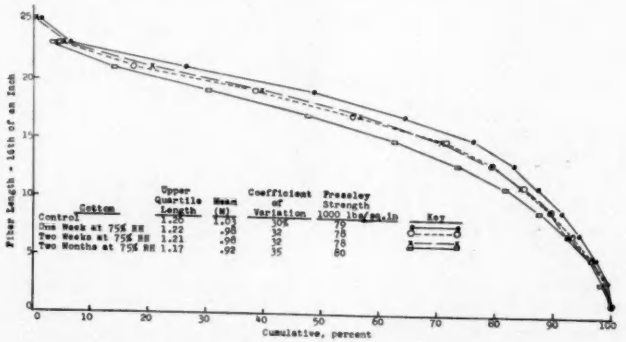

Cotton
Upper Quartile Length
Mean (M)
Coefficient of Variation
Pressley Strength 1000 lbs/sq.in
Key
Control 1.26 1.03 30% 78
One Week at 75% RH 1.22 .98 32 78
Two Weeks at 75% RH 1.21 .98 32 78
Two Months at 75% RH 1.17 .92 35 80
Fiber Length - 16th of an Inch
Cumulative, percent

FIG. 8. *Above and left.*

fecting cotton in storage. During winter months, progressive fiber damage has been observed in highly alkaline cotton (pH 9) unaccompanied by changes in pH or ESRM. This effect was reproduced in the laboratory with cavitomic cottons kept at low temperature. The experimental conditions were 50°F and 45% R.H., and 38°F and 75% R.H. With the advent of spring weather the most highly cavitomic bales in storage showed an increase in pH from 9 to 10.5 and an ESRM change from 0 to 3. Similar high values of pH had previously been observed in stored bales during the spring of 1950. Forty-five bales of this cotton selected for satisfactory physical properties and high cavitoma were subjected to actual mill test. Progressively inferior performance was observed during a 3-week run. Fiber strengths on samples from picker laps became progressively lower; the loss in strength was approximately 17%. It was concluded that this cotton was unstable.

Actinomyces, Penicillium, and *Aspergillus* have been found by the Department of Agriculture in a sample from the same lot used in the above mill test. The *Actinomyces,* in particular, are not commonly found in any large number in field-weathered cottons.

A limited number of 1950 cavitomic cottons were observed by the Department of Agriculture to have, in addition to *Actinomyces,* the anthracnose fungus (*Colletotrichum gossypii*) associated with "anthracnose tight-lock" [1, 11]. *Alternaria, Cladosporium,* and *Fusarium,* commonly associated with weathered cotton, were also present, as were unidentified bacteria.

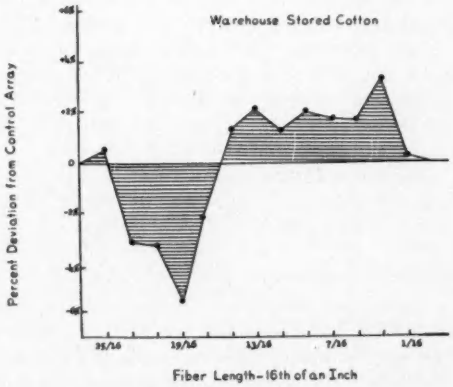


FIG. 9.

FIG. 10. (*Magnification, 830 ×.*)

In the course of our work, microorganisms, tentatively identified as *Actinomyces,* have been cultured and isolated from both raw cotton and commercially bleached and finished fabric following surface-sterilization by boiling. These particular microorganisms, as they are seen in the fiber lumen, are shown in Figure 5 (top), and also in the upper portion of Figure 4 of the previously published note [5]. The appearance of the microorganism taken from the culture medium is shown in Figure 10.

The low ESRM and high pH values associated with cavitoma within a relatively short time after ginning are not necessarily permanent attributes. Changes in pH as well as in residual sugars not accompanied by fiber damage might also be expected in the course of storage because of many kinds of air-borne microorganisms, both fungi and bacteria, which are not cellulolytic. Cottons of the 1948 crop tested this year did not fit into the pattern associated with cottons examined within 8 months of ginning. Many of these bales would be classed as cavitomic, based solely on appearance under the microscope

without the corresponing pH and ESRM values; in many others the reverse was found to be the case.

The abnormal swelling, and, in severe cases, the virtual disintegration of the fibers, as seen in caustic under the microscope, lead one to expect that this sensitivity to alkali would carry over into the finishing processes, most of which are alkaline. During the past 2 years, several instances of unusual loss in fabric strength have been brought to our attention. In these cases, a careful check revealed no divergence from normal finishing practices. Fibers from these fabrics exhibited the characteristic appearance associated with highly cavitomic fibers.

Vat-dyed fabrics are often classed as seconds because of neps which appear as light specks on a dark background [13]. Not infrequently, however, such fabrics are classed as defective because of small spots which are darker than the background. Fibers from the neps as well as from the dye spots have been examined in considerable number. The fibers drawn from the dye spots almost invariably have an appearance similar to that of the extreme cavitomic fiber, while those from the neps are predominately thin-walled or immature. Photographs of fibers taken from vat-dyed fabrics are shown in Figure 11.

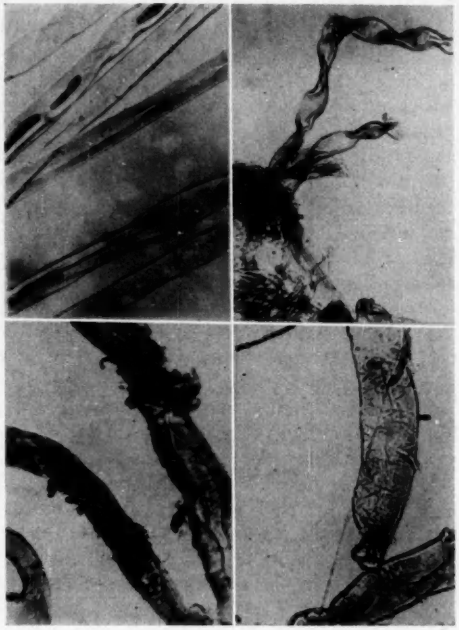


FIG. 11. *Fibers from vat-dyed fabric (magnification, 190 ×).* Top left—*Normal fibers.* Top right—*Thin-walled or immature fibers removed from neps.* Bottom (left and right)—*Typical fibers found in dark dyed spots.*

Methods

In the following methods, all values except those for ESRM, pH, and ionizable material are based on the dry weight of cotton.

Water-Soluble Reducing Material (ESRM Test)

One gram of cotton is thoroughly wet with 3 ml. of hot distilled water by kneading with a glass rod. Two and one-half ml. of extract is recovered by centrifuging; a wire basket holds the cotton off the bottom of the centrifuge tube. One ml. of the extract is treated with a Clinitest tablet (used in urinalysis for the determination of sugar), sufficient heat being generated to boil the solution. After 15 sec. the solution is diluted to approximately 15 ml., and the color compared to standard dextrose solutions similarly treated. Five standard solutions containing from 0 to 1.5 mg./ml. dextrose in 0.3 mg./ml. increments are used; values between standards are estimated. An extract with an ESRM value of 3 has the same color as the standard containing 0.3 mg. dextrose per ml.

This method of extraction does not remove all the water-soluble reducing material; however, there is a linear relationship, shown in Figure 12, between the ESRM value and the sum of the values found by repeated extractions of the same sample. Figure 12 also shows the relationship between the ESRM value and the total water-soluble reducing material, calculated as percentage of dextrose on cotton. There are undoubtedly reducing materials detected by this test which are not simple sugars.

There is a correlation coefficient of 0.95 for the dependence of ESRM on the copper number of raw cotton, with a standard error of estimate of 0.70.

Hydrogen-Ion Concentration (pH Test)

The one and one-half ml. of extract remaining from the ESRM test is measured for pH with Gramercy Universal indicator. Buffered solutions are used as standards. The results compare closely with those determined with a Coleman pH Electrometer.

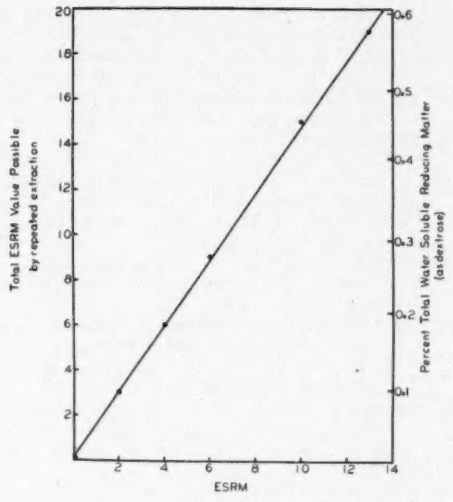


FIG. 12.

Ionizable Material

The ionizable material is measured by extracting 1 g. of cotton with 1 l. of distilled water and determining the conductivity of the solution with a Purity Meter, calibrated in p.p.m. as sodium chloride.

Water-Soluble Material

The loss in weight of 10 g. of cotton boiled for 15 min. in 1 l. of water and rinsed for 30 min. in running water is recorded as the water-soluble material.

Copper Number

The Schwalbe-Braidy method as modified by Clibbens and Geake [4] is used.

Pectin (Acid-Binding Capacity)

The method of Sookne and Harris [15] is used. No correction is made for the acid bound by the cations of the cellulose.

Benzene-Extractable Matter

Eight g. of cotton are extracted with benzene in a Soxhlet for 7 hrs. at a temperature which will maintain 20 siphonings per hr. The last 5 to 10 ml. of benzene are removed from the flask by nitrogen at room temperature. The recovered "wax" is dried over barium oxide.

The melting point of the "wax" is determined in a Fisher Johns melting point apparatus. The temperature at which the "wax" softens sufficiently to spread under slight pressure is called the melting point.

Summary

An increasing, and now large, proportion of the apparently good spinnable Middling cotton received by Kendall Mills is cavitomic. Cavitoma is characterized by bacteria and fungus inside as well as on the outer surface of the fiber. The observed values of pH and amount of reducing material are shown to be related to the percentage of cavitomic fibers within a sample. Simultaneous high values of pH and low values of ESRM, and microscope observation provide a satisfactory diagnostic test. The relations found to exist among the noncellulosic constituents permit classification of cottons into a "normal" group, which falls along a straight line relating the amount of ionizable material to copper number. The cavitomic cottons lie together in a group to the left of the normal line. A shortening of staple length resulting from a weakening of the fibers becomes apparent as a result of combing in the stapling operation. Observations in progress on warehouse-stored cottons show changes which parallel those produced under controlled conditions in the laboratory. There is evidence that the sensitivity to alkali may have an effect on the quality of the finished product; dark spots in vat-dyed fabrics are associated with cavitomic fibers.

Conclusions

The implications of cavitomic cotton are of sufficient import to warrant bringing the subject to the attention of industry and the Department of Agriculture. Our experience shows that present fiber testing methods are inadequate to cope satisfactorily with cavitomic cottons. While it is assumed that the ecologic balance will change, in the meanwhile there is much to be investigated. These problems divide into two major groups: the significance of the phenomena to the mills; and the identification and control of the causal agents. Work in these laboratories addressed to the first is being continued; the Department of Agriculture has undertaken a vigorous attack on problems in the second group.

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Apparatus for Evaluating Warmth of Textile Fabrics*

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Abstract

A semi-automatic apparatus requiring minimum operator attention has been assembled for measuring the thermal transmission of fabrics while subject to moving air at constant temperature. The apparatus employs the principle of measuring the difference in the amount of energy required to maintain constant temperature in a body when bare and when covered with the test specimen. Conditions have been set up with an air velocity of 12 to 13 m.p.h. so that performance under fairly severe conditions of use can be approximated. Results are expressed as "thermal efficiency." Formulas are given for converting to other units as desired. The apparatus has been tested with a variety of fabrics ranging from thin, plain-weave, nylon cloth to heavy woolen blankets, and has been found to differentiate among them in a manner that apparently takes into account the various fabric properties.

WARMTH, an important service requirement of many textile fabrics, is a difficult property to evaluate. Many techniques have been developed for measuring it [2, 8] but, because of the complexities of the factors involved, no one method has received general acceptance. Fabrics are heterogeneous masses of fibers with pockets of dead air interspersed throughout. It is believed that these air pockets are largely responsible for the thermal insulating value of the material, with the fiber itself playing a subordinate role. The size, shape, number, and frequency distribution of these pockets are largely determined by the fabric construction [3]. But their effectiveness is, in part, subject to such conditions of use as air movement and direction, compression of the fabric, and effects of laundering and wear to which the fabric has been subjected in the past.

A recent report by Winston and Backer [8] discusses the factors that influence the loss of heat through fabrics, reviews previous evaluation work, and records the results of interlaboratory comparison tests conducted under the auspices of the American Society for Testing Materials, Committee D-13. Their report shows that the most generally accepted method for measuring the thermal insulating value of a fabric is to determine the difference in energy required to maintain a warm body at constant temperature when bare and when covered with the test fabric. Although it is well recognized that conditions of test which disturb the dead-air spaces in the fabric or change their size and distribution may have an important influence on the thermal insulating value of a fabric, there is considerable lack of uniformity in the conditions established for testing by the seven different methods employed in that study. Also, there is great diversity in the final expression of results. Consequently, the different laboratories showed little agreement in absolute values, but remarkably good agreement in ranking the fabrics.

In the light of these results, standardization of equipment and techniques appears pointless until other conditions of test based on correlation with actual field exposures are included in the evaluation program. Meantime, any laboratory requiring a test for warmth of cloth must either devise its own method or arbitrarily select one from those already developed.

The apparatus described here was designed for ranking the insulating value of experimentally developed cotton fabrics. In general plan, it is most similar to the apparatus developed in the J. C. Penney

* Report of a study made under the Research and Marketing Act of 1946.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Laboratories [8], but it has several features designed to improve control of the test conditions, to increase the sensitivity of the test, and to provide a simplicity of operation requiring minimum attention.

Description of Tester

The apparatus is shown in Figure 1 and the electrical circuit in Figure 2. This apparatus measures the heat transferred during a fixed time interval from a cylinder maintained at approximately body temperature in an atmosphere of moving air of approximately freezing temperature, with and without the cylinder covered with a sleeve of the test fabric. The difference in energy values is taken as the measure of the insulation value of the fabric.

The warm body is a solid aluminum cylinder 12 in. long and 4 in. in diameter turned down to a smooth surface which has been anodized and dyed black. Heat is supplied by six cartridge-type resistors, each 4 in. long, inserted into holes drilled into the end of the cylinder. To provide as uniformly a heated surface as possible, the resistors are connected so that each heater dissipates the same amount of energy. To smooth the heating cycle further, a minimum of 25 watts is supplied to the cylinder, while a maximum of either 110 or 210 watts is available, depending upon the requirements of the test fabric. At no time do the resistors dissipate more than one-fourth of their rated 150 watts each. This provides for long life for the heaters and minimizes the temperature gradients within the cylinder. The temperature of the cylinder is measured and controlled by means of an iron-constantan thermocouple located midway in a hole drilled along the length of the cylinder and $\frac{1}{4}$ in. from the surface. The lower end of the cylinder is insulated with fiber board 1 in. thick, and the upper end with mahogany 6 in. thick. Calculations indicated that heat losses through the ends are negligible compared with losses through the test specimen. The cylinder is connected to the control assembly by a shielded flexible cable containing the necessary power and thermocouple leads. The connectors on the cable are of the "Army-Navy" type and are equipped with a set of iron-constantan terminals, thus allowing the thermocouple wires to be extended to the recorder without any connections of dissimilar metals.

The cold chamber is a commercial, household freezing unit of 8 cu. ft. capacity. In a room of approximately 75°F, a chamber air temperature of approximately 32°F may be maintained with a dissipation of 200 watts within the compartment. The relative humidity of the cold chamber was observed to be approximately 30%.

In the cold chamber, a $\frac{1}{20}$th h.p. blower fan has its outlet connected to a sheet-metal tank 15 in. wide, 34 in. long, and 5 in. deep, which, in turn, is connected to a sheet-metal tube $7\frac{1}{2}$ in. in diameter, painted black inside and out. The aluminum cylinder passes through the top of the cold compartment and is inserted coaxially within this tube so that the air flows uniformly and axially but turbulently across the specimen. A wind velocity of 12 to 13 m.p.h. is maintained, but lower velocities are possible by the reduction of the inlet area of the blower fan.

An iron-constantan thermocouple, shielded against radiation from the aluminum cylinder, is inserted into the air stream just below the cylinder. This thermocouple measures and controls the temperature of the cold atmosphere.

A draft gage on the control panel indicates the mean velocity of the air flowing past the cylinder by measuring the drop in pressure of the air from the bottom end to the top of the cylinder. The rather high velocity employed in the present assembly is believed advantageous because it simulates conditions of use when the protective function of clothing against winds and drafts is particularly needed. Also, with higher wind velocities, the percentage of heat lost by radiation becomes smaller and that lost by convection becomes larger. For example, at 12 m.p.h. and 32°F, Burton [4] gives the relative heat losses as 88% by convection and 12% by radiation, whereas at very

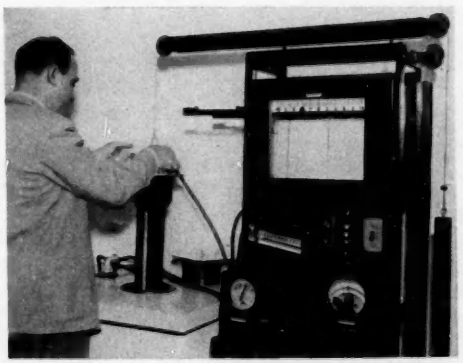

FIG. 1. *Apparatus for evaluation of thermal insulating value of fabrics.*

low wind velocities, such as 0.2 m.p.h. and 32°F, the losses are approximately 60% by convection and 40% by radiation.

The potentiometer serves to control, measure, and record the temperatures of the warm body and of the surrounding cold atmosphere. Each temperature is recorded every 30 sec. The potentiometer controls the temperatures through the use of mercury switches which, as shown in Figure 2, actuate "off-delay" pneumatic-type relays. The method of operation is as follows: If the cylinder temperature is above the present value, the mercury switch, C_5, closes. This actuates the relay, Rl_3, immediately reducing the amount of energy supplied to the cylinder. Although this relay is deactivated when the recorder pen moves to measure the cold temperature, because of the pneumatic delay feature, the power supplied to the cylinder remains at the lower level until the preset time interval has elapsed. In practice, this interval is usually made just equal to 30 sec., the time required for the recorder to complete its cycle. Thus, if the cylinder temperature is sufficiently reduced, the relay is not activated, and full power is again supplied to the cylinder. A similar analysis can be made for the

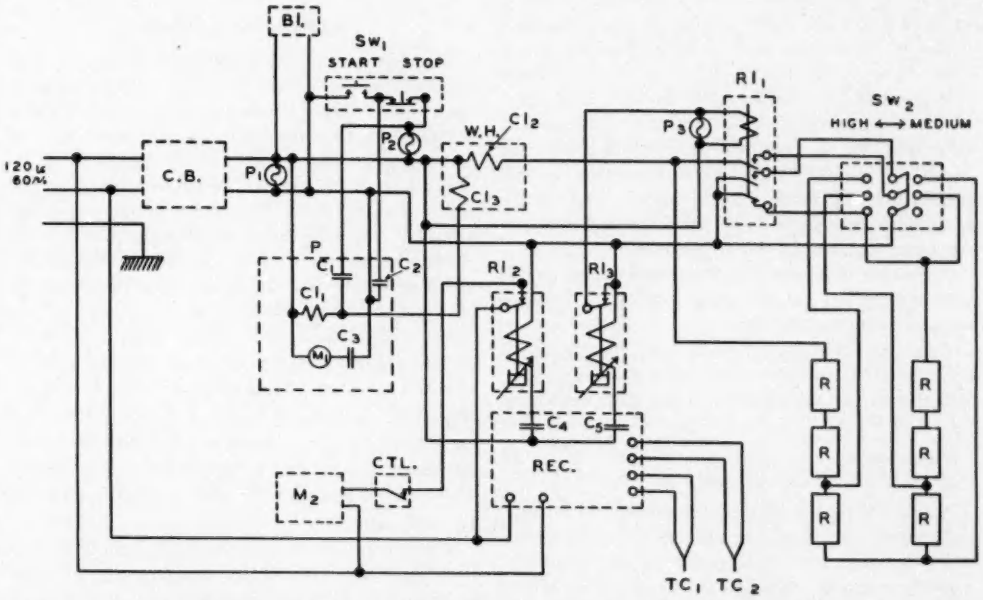

FIG. 2. *Schematic diagram of electrical circuit of thermal transmission measuring apparatus.* C.B.—*Circuit breaker, 4 amp.* Bl.—*Blower fan in cold chamber, $\frac{1}{30}$th h.p., 1725 r.p.m.* Sw_1—*"Start-stop" push-button assembly.* W.H.—*Watt-hour meter, appliance type, 115 v., 15 amp.* Cl_2—*Current coil.* Cl_3—*Voltage coil.* P—*Process timer, adjustable 2 hr. max.* M_1—*Timing motor.* Cl_1—*Clutch coil.* C_1—*Time opening, normally closed contact.* C_2—*Clutch coil contact, normally open.* C_3—*Limit switch for motor overrun protection, normally closed.* Rl_1—*Heat control relay, 115 v. coil, 2 normally open, 1 normally closed contacts.* Rl_2, Rl_3—*Pneumatic off-delay relays, 115 v. coils, normally closed; pneumatic delay adjustable from 5 sec. to 3 min.* Sw_2—*Heat selecting switch, 3-pole double throw.* R—*Cartridge-type heaters, 1500 watt, 115 v.* M_2—*Compressor motor for cold chamber.* CTL.—*Temperature control as furnished with cold chamber; assumes command when Rl_2 not operating.* REC.—*Fast-speed potentiometer, 2-point recording, sensitivity 2–0–2 mv.* C_4—*Mercury switch, normally open, closing when air temperature drops below preset temperature.* C_5—*Mercury switch, closing when cylinder temperature exceeds preset temperature.* TC_1, TC_2—*Iron-constantan thermocouples measuring cold and hot temperatures, respectively.* P_1—*Pilot lamp, 115 v., indicates apparatus in stand-by.* P_2—*Pilot lamp, 115 v., indicates a test is being made and that watt-hour meter is recording.* P_3—*Pilot lamp, 115 v., indicates that the selected high power is being drawn.*

operation of the relay controlling the compressor unit. Here, the relay is activated only when the air temperature in the box is lower than the preset value. When this relay is activated, the compressor is switched off. However, due to the characteristics of the sealed compressor unit furnished with this box, which requires that a suitable time interval elapse before again switching on the compressor, the time delay for the "cold" relay is set at 3 min. The cylinder is controlled within $\pm 1°F$, and the cold air temperature within $\pm 2°F$. The respective mean temperatures in use are 99.5°F and 35.7°F, respectively.

The watt-hour meter measures the energy required to maintain the aluminum cylinder at a constant temperature. In addition to the usual small accumulating dials, the meter has a large dial which allows readings to be estimated to tenths of one watt-hour. Its overall accuracy is given as within 1% [1]. The meter is connected with the potential coil on the line side, and therefore its consumption does not have to be subtracted from the reading of the meter. The energy lost in the current coil is negligible for the range of currents employed in this apparatus.

A process timer controls the potential coil of the watt-hour meter, and permits presetting the time interval desired for the test.

As an aid in lifting the warm body in and out of the apparatus, a counterweight and a segment of a sliding-door rail are attached to the control rack, as shown in Figure 1.

Test Procedure

A sleeve of the test fabric approximately 14 in. long and exactly 12¼ in. in circumference is prepared by laying the fabric out on a large flat surface, smoothing it gently, marking a rectangular section 12¼ by 14 in., cutting it out carefully, and finally stitching along the 14-in. side with a butt-seam sewing machine. The specimen must be fed to the sewing machine so that when opened as a sleeve, the two edges join so that there are no gaps or overlapping along the seam.

Presuming that the energy required to maintain the cylinder at the predetermined constant temperature when bare has already been determined, the sleeve is then slipped on the aluminum cylinder and smoothed so that there are no wrinkles or air pockets under it. The cylinder with the test specimen is then lowered into the cold chamber.

When the "hot" and "cold" temperatures have become stable, as shown by the recorder, the test is initiated by pushing the "start" button, thus activating both the timer and the watt-hour meter. At the end of the time set for the test, the meter is automatically cut off and its reading taken at the convenience of the operator. Even though the test interval has elapsed, equilibrium conditions are maintained until the machine is shut down. This permits making successive determinations with the same specimen. Present practice is to take the average watt-hours of three successive 1-hr. tests as the energy required to maintain the warm body at constant temperature.

Expression of Results

The literature on the thermal properties of fabrics is complicated by the use of various units for expressing results. Many of these are such that it is impossible to convert from one system to another either because of the lack of information furnished or because some of the units are subjective or physiological rather than physical. The choice of units is rather arbitrary, engineers being more accustomed to use British thermal units whereas physicists and physiologists generally use calories. Other investigators have proposed the "clo" [6] and the "tog" [7] as more practical units for clothing fabrics. There is not even agreement as to whether results should be reported in terms of transmission or its reciprocal, resistance. Fourt and Harris [5] prefer the latter for clothing fabrics because the individual resistances can be added together to estimate the total resistance when several layers of the same or different fabrics are used.

With the present apparatus, results are obtained in watt-hours and may be converted into other units as desired. "Thermal efficiency" has been selected as a simple, straightforward expression for ranking different fabrics, allowing conversion to any other type of unit desired. It has the further advantage that moderate variations in air speed or other test conditions would be expected to have less effect on its value than on absolute units, since these variations have a similar effect on both the bare and covered cylinder.

"Thermal efficiency" is defined as

$$E = \left(\frac{W_B - W_C}{W_B} \right) 100,$$

where E is the thermal efficiency, W_B is the number of watt-hours consumed when the cylinder is bare, and W_C the number consumed when it is covered with the test fabric. The relationship of thermal efficiency to some of the other commonly used terms is shown below:

Resistance Units—

$$(1°F)(hr.)(ft.^2)/B.t.u. = \frac{11.3}{100 - E}$$

$$(1°C)(hr.)(m.^2)/kg.\text{-}cal. = \frac{2.32}{100 - E}$$

$$1 \text{ clo} = \frac{12.9}{100 - E}$$

$$1 \text{ tog} = \frac{20.0}{100 - E}$$

Transmission Units—

$$1 \text{ B.t.u./ft.}^2\text{/hr./°F} = 0.0885\ (100 - E)$$

$$1 \text{ kg.-cal./m.}^2\text{/hr./°C} = 0.432\ (100 - E)$$

The relationship between efficiency and thermal transmission is not linear but is such that differences among fabrics in the low-resistance range are magnified by the use of thermal efficiency as the reporting unit, whereas the reverse is true for heavy fabrics such as blankets.

Table I shows typical data for the efficiencies as obtained in tests of 19 fabrics of various constructions and fiber compositions. The related properties of weight, thickness, and air permeability, determined under standard conditions, are also given.

The thickness was taken at 1 lb./sq.in., using the conventional Schiefer Compressometer, with presser foot 1 in. in diameter. Air permeability was measured by the Gurley Permeometer, at a pressure drop across the fabric of 0.5 in. of water. Although these methods for determining air permeability and thickness of fabric are generally accepted procedures, it must be noted that the values obtained are not necessarily those prevailing under the conditions of this warmth test, particularly when compressible materials such as blankets or other napped fabrics or when stretchy fabrics are involved. For correlating warmth with these physical properties, it is therefore desirable to select or devise test procedures with corresponding conditions, as is being done by some other investigators [5].

Due to the limited amount of sample material, the efficiency values presented in Table I are based on determinations from single specimens and must therefore be considered as merely illustrative of results to be obtained with the apparatus. In other tests,

TABLE I. THERMAL EFFICIENCY AND PHYSICAL PROPERTIES OF SPECIFIED FABRICS

Fabric	Efficiency (%)	Weight (oz./yd.²)	Thickness (in.)	Air permeability (ft.³/min./ft.²)
1. Plain weave, nylon	6.5	2.9	0.004	4
2. Satin lining, rayon	12.0	3.1	0.004	50
3. Satin lining, rayon	12.5	4.1	0.004	25
4. Poplin, cotton	15.0	6.2	0.010	4
5. Twill, rayon and nylon	22.0	9.2	0.018	22
6. Twill, rayon and nylon	26.5	9.5	0.019	20
7. Interlining, cotton, napped (napped side in)	42.0	5.9	0.026	154
8. Lining, wool interlining stitched to satin				
Satin out	59.0	12.6	0.058	34
Satin in	54.0	12.6	0.058	34
9. Frieze, mohair, unfinished	70.0	15.2	0.105	97
10. Blanket, cotton	63.0	5.1	0.030	181
11. Blanket, cotton	68.5	7.4	0.063	194
12. Blanket, cotton				
Single layer	62.2	4.8	0.036	226
Double layer	70.0	9.6	0.062	124
13. Blanket, 90% rayon, 10% wool	77.5	13.6	0.135	184
14. Blanket, 95% cotton, 5% wool	78.0	12.5	0.120	173
15. Blanket, wool	73.5	11.0	0.084	302
16. Blanket, wool	76.0	11.6	0.097	277
17. Blanket, wool	77.5	13.0	0.102	230
18. Blanket, wool	79.5	21.0	0.139	78
19. Blanket, wool	80.0	13.2	0.138	145

where duplicate specimens were tested, good reproducibility was obtained, the difference in efficiency being less than 1%.

The fabrics represent a range in weight from approximately 3 to 21 oz. per sq. yd. and a range in efficiency from approximately 6% to 80%. They differ so widely in fiber composition and construction, however, that few conclusions regarding the relationship between these properties and thermal transmission should be drawn. It can be noted that the fabrics appear to arrange themselves in accordance with their expected behavior in use—that is, the efficiency generally increasing with increase in either weight or thickness. The lightweight, unnapped constructions are the least efficient fabrics. It can also be noted that under the moving-air conditions employed in this test, thickness alone is insufficient to rate the fabrics according to warmth—which is contrary to the finding of Winston and Backer [8] for still-air conditions. The importance of construction is well illustrated by the mohair frieze, fabric No. 9, which is a relatively thick, heavy fabric. Its inferior efficiency under moving-air conditions in comparison with blankets of comparable weight and thickness can be attributed to the relative inability of the very open loops on either side of the dense base construction to entrap air. Another example of construction effects is shown by the behavior of the wool interlining stitched to a satin outerlining, fabric No. 8. The greater efficiency with the wool interlining next to the warm body instead of the satin is undoubtedly due to the windbreaking effect of the satin, which permits greater air entrapment by the interlining.

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Industrial Research and the Consumer Target*

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IN THE TEXTILE INDUSTRY the target of research is the ultimate consumer. Favorable consumer reaction to a changing array of products is the goal of product development. To government, the consumer represents a responsibility for protection. To advertising and merchandising, the consumer appears as an opportunity for group influence. The director and administrator of industrial research must, however, see the reaction of the consumer as a part of a planned process of industrial change.

Industrial-research administration and industrial executive management have the responsibility and almost exclusive opportunity to recognize the ultimate consumer as a partner and target in a stimulating and continuous adventure in progress. This new partner in a spiral of progress must, by well-planned mechanisms, be introduced into the adventure at the right point in time and where his contribution will be most effective and helpful. In this discussion, therefore, of the impact of consumer reaction on research programs, we must consider the whole pattern of industrial research and its organization. We must include the consumer in this pattern. We must, however, avoid over-emphasis on the techniques we use lest the mechanisms for measurement and recording consumer preferences cloud the value of partnership with the consumer in the development programs.

Industrial Research Pattern

Industrial research has come of age. Its place in the organized pattern of industrial operations is no longer a subject of debate, for its strength and value have become apparent. There is no longer doubt that the allocation of a part of industry's income to research buys insurance for the future and catalyzes industrial growth.

All of us have participated in discussions of the organizataion and methods to be used for more effective research. No doubt we all have had the experience, in discussing the conduct of research, of seeing the discussion follow a certain path. At the beginning, there is a general assumption that the words used to define the various sections of the research organization—as, for example, fundamental research, applied research, and development work—are all reasonably clear and define adequately all sections of the research pattern. The ideas which are presented at first appear to have little opposition. Gradually, however, there appears evidence of misunderstanding of the relationship of these ideas to the general scheme of research and its various sectors of action. At that point, progress in the discussion ends and the group tends to spend its time describing the various functions of basic research, applied research, and development. The discussion degenerates into attempts to distinguish between fields and to define the importance of fundamental and basic research, applied research, development, standardization, quality control, market research, process research, and consumer-reaction studies as though such distinctions are a requirement of research progress. Actually, these distinctions between the parts of a mechanism may be necessary to the mechanic assembling each part, but they are not of moment to the operator and director of the machine. We must stop attempting to build fences around the various research and development functions. The elements of research, from the most basic science to the most directly applied consumer evaluation, are all parts of a mechanism of progress which needs integration and direction. These parts of the research and development machine are never located all under one roof. The basic-science area of knowledge which may strike a spark in human thinking may be located at a university. It may have the form of a teacher, or a student, or a group of scientists in group-supported research institutions. The applied science may be the work of a lone inventor or of an industrial-research group. The development of test methods may be aided by engineering groups in societies such as the American Society for Testing Materials and the

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British Standards Institute. The producer of equipment may contribute through new machine design. The material source may aid through quality control. The salesman may deduce new definitions of wants. The social scientist and the economist may have an influence. Finally, the consumer, if given an opportunity to distinguish between something he knows and a new possibility or a new product, may redirect the development into new channels. One cannot put quantitative measures on the relative value of these contributions, nor can one put fences around the contributors. We must, however, describe the total operation for our own charting of aim, and describe the part each of these elements plays in the research pattern creating value to the consumer and thus to public welfare.

This research pattern is new but it is no longer illustrated by the work of a single inventor or of a single research group. Invariably, as one studies the history of the development of rayon, of nylon, of the development of electric light and power, of radio and television, and of the automobile and the airplane, it becomes evident that the level of success attained by these progressively improved areas of progress was the result of the combination of many forces in our industrial and consumer pattern. They reached their present form of value only through a long pattern of interaction between research and development, manufacturing, and consumer areas of knowledge. The efforts of the fundamental scientist studying the laws of nature—the structure of wool fibers, for example—become linked in this research process with the efforts of a chemist attempting to destroy the memory of the fiber for a previous form and to create a different yarn form. The fabric designer, the colorist, the salesman, and the stylist all add their bit in developing a fabric. The consumer reacts perhaps with reservation, which leads to new efforts in the laboratory and a further search for fundamental knowledge, new yarn structure, new fabric design, new consumer reaction, and more and better fabrics and textile products.

Elements of Research Process and Integration

How should we describe the research process? It seems to be a helix or spiral of growth. The path circles around the areas of activity of scientists in their search for basic knowledge, applied scientists in industrial research, engineers in design and production, managers, executives and workers in group manufacturing, development and promotion men in distribution and sales, and consumers and users. The path circles back again but keeps rising above the initial area of knowledge and forming a spiral rising always upward. Left behind, and usually forgotten, are the original sources of knowledge. There is no time to look back. The pace is much too swift.

The consumer, of course, plays a real part in this spiral of progress. Because he has had an opportunity to choose between products, his wants have indicated new directions for research. There are many examples of this process in textiles. The introduction of natural-silk fibers gave the consumer an opportunity to show a preference for fabrics of silk in stockings, luxury apparel, and dresses. The cost and scarcity of silk fibers stimulated the development of "artificial silk," but it was not as a substitute for silk that the man-made fibers of rayon made history. As they have been improved in quality and varied in structure they have made cotton their major enemy, and even wool is under attack. In a recent report of U. S. fiber consumption, it is significant that in 12 years the man-made fibers have risen from 10% to over 21% of fiber usage. Cotton and wool per capita consumption has not decreased, but the products of research and industrial management—the man-made fibers—have opened up new markets by meeting wants of the consumer in the form of new fabrics and thus contributing to the present high demand for all kinds of textile fibers.

It should be noted that the consumers' wants in this period of change did not direct the original effort. As each development was made and the wants of the consumer were expressed with regard to new materials, new inventions offered to him were used as a guide to further inventions, developments, and production offered for new choice and reaction, and so on, ad infinitum. The textile industry and its research scientists and engineers fully appreciate the impact of textile development on style. New developments of fibers offering texture changes in fabrics and changes in sheen, in smoothness, in drape, in lightness or sheerness, and in warmth or coolness develop into style features which, like a chain reaction, bring out new possibilities and new wants. The new want, the new style, can only be expressed when the new possibility is presented by actual sale and distribution. Research, in its broadest meaning, is a part of the industrial process in

which a new rearrangement of ideas in the form of product is aimed and discharged in the direction of the consumer and he, as an articulate target, indicates how successfully the bull's-eye has been hit. The consumer helps us to reset our sights.

Normally, there is a period of time in the development of a new-product possibility when estimates of consumer wants can be sought somewhat prior to the actual offering of the product for sale. During this brief time period, methods of measuring consumer reaction should be promoted and used. Methods of obtaining probable consumer reactions are no substitute, however, for the initiative, imagination, devising, analyzing, discussing, and experimenting of the basic scientist, applied scientist, engineer, production man, and salesman in presenting new products to the consumer.

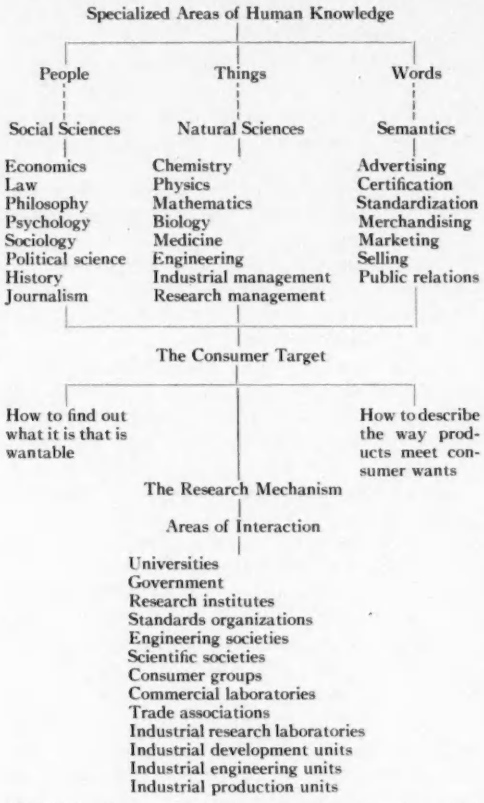
Technical progress in the textile industry made new records in 1950. This record has been well covered in a report by J. P. Goldberg presented in January at a meeting of the American Association of Textile Technologists, and, in more detail, in "Review of Textile Research and Development During 1950," prepared by the staff of Textile Research Institute (TEXTILE RESEARCH JOURNAL **21**, 293–373 (May 1951)). This progress in the textile industry was predicted by Roland P. Soule some years ago. He suggested that the era from 1940 to 1960 would be identified as the period of development of the fabricating industries. In this period, Soule stated, the fabricating industries (of which textiles is one of the largest) would learn the technique of combining the sciences—electrical, mechanical, chemical, and physical—and integrating them with consumer wants in their industrial-research effort. The combination of applied science in industrial laboratories is only a part of the integrating effort.

Particularly in those industries bringing products to the consumer, the integration must be expanded in many areas of knowledge. The work of the applied scientist and engineer in industry needs the support of those working on more basic problems of the natural sciences in universities and in research laboratories such as Shirley Institute, Torridon, Textile Research Institute, Leeds University, Manchester College of Technology, the U. S. Department of Agriculture Regional Research Laboratories, the Institute of Textile Technology, and many others. Industry must gain knowledge from engineering developments in production and from experience in the sales and advertising of products in use; it must use types and classifications of knowledge in its integration of the research effort. Until recently, some classes of knowledge were not considered a dynamic part of the research mechanism. In a paper presented in 1947, the present author suggested that a description of these specialized areas of human knowledge was encompassed by three words—people, things, and words. Under these three words could be classified the whole effort of creating products that were wanted, distributing them, and explaining what want was being met by the products that were new and unfamiliar—for example, fabrics from new man-made fibers, novel textures from a new way of processing natural fibers, or new effects from methods of adding crimp to natural fibers.

At the time the broad classification of people, things, and words was presented, it appeared that human knowledge (classified by the social sciences, the natural sciences, and semantics) had as its target the consumer (how to find out what it is that is wantable and how to describe the way products meet consumer wants). The concept of grouping of industrial activity into two parts has since been revised. To the grouping of specialized areas of human knowledge and the listing of the parts of the research mechanism must be added the ultimate objective—the consumer, meeting his wants, and methods of offering to him the new possibilities for his choice. An attempt has been made to picture these relationships in Chart I.

Perhaps the classification suggested in this chart is at least the start of a graphic method of orienting into the industrial process the specialized areas of knowledge and the mechanism of research. It does not describe the process of research and the methods of operation of the mechanism. It does not describe the actions of the directors of the several parts of the mechanism and the managers of the larger units. It does not indicate the paths of coordination and collaboration between these areas of interaction. Such a description is not only difficult in words, but is almost impossible in graphic form since it appears to be action in the form of a spiral or helix and is therefore graphically three-dimensional. The elements of the process are suggested in circular form in Chart II. It is necessary to imagine the circle as never being joined but continuously being lifted by new knowledge above its starting point, wherever that may have been on the circle.

CHART I. THE DYNAMICS OF INDUSTRIAL PROGRESS



In industrial operations, knowledge and mechanisms require organization and assignment of responsibility and authority if they are to effect a continuous translation of ideas into process and product change. A great deal of thought has been given to the problems of "selling" industrial executives on the value of organized research, both fundamental and applied. Discussions of these problems are a part of almost every meeting of research scientists. The conclusion that research men are either naive or lack broad vision must be in the minds of executives in industry and, therefore, constitutes an obstacle to selling them on research. Executives know, even if research men do not appear to understand, that the limited meaning of "research," as commonly used, actually defines only part of the many units and individuals who make significant contributions to changes, improvements, and the introduction of new products. To properly "sell executives on research," it is necessary to show the breadth of understanding and of operational planning which brings into the industrial research orbit all of the elements contributing to change. Research must no longer, even by implication, be assumed to encompass only the ivory towers of fundamental studies or the exciting areas of applied science in the laboratory. Research management must, by plan of organization and methods of operation, include as dynamic forces all parts of the areas of knowledge, all elements and units in the mechanism of research, and, finally, the contributions from all parts of the process of developing, producing, and distributing products to consumers, as suggested in Chart II. The consumer, his wants, and methods of informing him of change are essential parts of this broader concept of research in the textile industry. This extended concept of industrial research cannot be stimulated and adequately directed at levels of authority and management responsibility below those existing for the other broad industrial functions—namely, production, finance, material supplies, and sales. The responsibilities required are not those associated with a director of research, but rather with a vice-president in charge of the programs which result in the process and product of the future.

Activities in Assaying Consumer Wants and Reactions

Consumer-reaction studies should not be a process that tells the research mechanism what to do; they may help indicate what not to do. They are experiments in seeking new knowledge and, in general, have not been validated fully by experience. It has long been recognized that it would be desirable to have an efficient technique, such as a questionnaire, a panel, or a method of polling, which would tell what is wanted by the people. The prediction of how people intend to vote was an early goal of the scientific method of sampling opinion. The methods have had some success, but an outstanding failure in a presidential election has made its proponents scurry for more knowledge of uncontrolled variables in polling methods.

In the U. S. there is evidence that scientists have

CHART II. THE PROCESS OF MAKING CONSUMER PRODUCTS

recognized the need for research and development of scientific methods which chart programs for determining group consumer opinion. Action groups have been organized at the highest levels of science and in the engineering areas. Several years ago, the National Research Council and the Social Science Research Council joined forces in a committee, under the direction of Samuel A. Stauffer. This committee, on measurement of opinion, attitudes, and consumer wants, supports such research at Princeton University and elsewhere.

Its members are cooperating in experimental studies in the engineering and applied-research areas and are currently reporting progress. The American Society for Testing Materials also organized an Administrative Committee on Ultimate Consumer Goods, under the direction of Professor Herbert J. Ball of Lowell Textile Institute. This committee has developed methods of presentation of test methods on consumer goods and is advising A.S.T.M. committees concerned with consumer-goods standards. A subcommittee of Professor Ball's group, under Paul

Olmstead of Bell Telephone Laboratories, is continually making surveys of means for determining consumer wants for specific items in order to be in a position to render advice to A.S.T.M. committees. Recently, Olmstead's group cooperated in an advisory capacity with the Research and Planning Section of the Textile Division of the U. S. Army Quartermaster Corps in planning a program for evaluating the reactions and preferences of Army officers to some 8 types of fabrics made into summer uniforms. The details of this test program will undoubtedly be presented to the Society in the coming year. It will illustrate the extreme complexity of studies of this type and the reason they may not become a large factor in civilian consumer-preference studies.

There are many other technical and consumer-commercial groups active in searching for ways to assay the wants of the consumer and to help educate the consumer on the attributes of the products offered for sale. This latter area of activity is called "consumer standards" work, a phrase that seems highly misleading and, in fact, an obstacle to an accurate presentation of the process which gives the consumer what he wants. Someone should invent a few descriptive terms that define the true purposes of this area of effort. It should be a phrase including the goals of: (1) finding out what attributes in products are the most important and are the real basis of satisfaction in purchase; and (2) finding methods of describing to the consumer how the products offered do meet the basic and important wants and perhaps warning against the purchase of a product for wants for which the product was not designed and developed.

It is the second goal that has been miscalled "consumer standards." It needs a new definition. If it were newly defined and oriented with emphasis by both industrial-research management and consumer-research areas into the research process, it would become a truly active part of the research mechanism and a major contribution to our areas of knowledge. It would develop into a scientific contribution to progress rather than remain a less realistic area of apparent contention between producer and consumer.

In order to serve the public and the consumer well, studies of wants and planned consumer education on the attributes available in products must become a force for progress. Such a force, to be effective, cannot combine legalistic contention and mutual collaboration. Knowledge, mutually exchanged, which leads to progress will not flourish in the same atmosphere with legal, punitive, and protective policies. These two diametrically opposed efforts must be physically separated in consumer education and organization. The positive policy of consumer-retailer-manufacturer education must be supported independently and be clearly distinguished from the consumer-government-manufacturer programs of protection of the public against misrepresentation in advertising, labeling, and selling. The term "consumer standards" is an inadequate term for these two consumer-manufacturer efforts.

The restrictive impact of standards is illustrated by the development of minimum standards of washability and pressing. Progress is generally associated with the recording and publication of standards for these and other short-range wants. Such standard methods began with cotton fabrics in mind and with the assumption that future fabrics must, to be considered washable and pressable, be satisfactory when the standard methods are used. Were these standards a basic want of the consumer? Cheers for research—it didn't believe it. Fabrics are offered for sale made of rayon, wool, and synthetic blends—of nylon and of dynel—and other combinations of fibers which must be washed and ironed by entirely different techniques, using care and special methods. Have these invalidations of so-called minimum standards restricted the purchase and use of the materials? No! When the consumer is made aware of requirements for lower temperature of washing solutions and irons and of this or that revised method of maintenance, an opportunity is given for choice of wants. If the fabric meets other more significant wants in style, utility, or economy, the standard of washing and ironing becomes unimportant and is discarded or may be revised to include new techniques of maintenance. In some instances—for example, with wool fabrics—the consumer wants are met with greater satisfaction by processes which permit washing without severe shrinkage. These improvements in meeting wants may stem from a long period of fundamental research in chemistry and applied research in chemical and process development, and of engineering development of manufacturing facilities and equipment.

There are developments in consumer-retailer-manufacturer relations in the U. S. that indicate wide support of a more realistic and far-sighted policy being promoted by leaders of consumer groups.

The National Consumer-Retailer Council, Inc., of New York, under the leadership of its Managing Di-

rector, Ruth W. Ayres, has organized programs which bring together, in conferences and through informative publications, leaders of consumers, retailers, production, and industrial research. At conferences in the past few years these groups have exchanged views which appear to promise new methods of combining all interests in better products for the consumer. It will be in this type of effort that the public will be helped to appreciate that the differences in product lead frequently to new desires and the fulfillment of new wants. Lighter-weight fabrics may, in their first presentation, appear in conflict with some established standards of weight, strength, and durability. If, as has occurred frequently, these fabrics fill wants in comfort or health or beauty, the weight, strength, durability, ease of ironing, and other old standards are no longer valid.

The American Home Economics Association sponsored a 5-year project called "The Consumer Speaks," during which thousands of consumers gathered, discussed, and voted on what characteristics they wanted in certain commodities. More than 3 million families are studying wise buying practices under the Extension Service of the U. S. Department of Agriculture. The National Consumer-Retailer Council also conducted a marketing survey covering what consumers actually bought of one type of product and recorded what they looked for in these goods and whether information about these characteristics was available at the point of sale. We must regard with favor and actively support all such research and the contribution it will make to the dynamic spiral of the research process.

Research on consumer wants makes the consumer a partner in the development and improvement of products, and often suggests new products. Studies of consumer reaction to new products make their major contribution, however, as an aid to the decision of industrial research management, executives, and investors to support with capital outlay the facilities for production in volume of products and processes rising from the research process. The cost of new facilities is increasing each year. New methods are needed to assist in judging the degree of capital risk. Attempts to assay consumer reaction in advance of investment are methods of reducing this risk.

Techniques in Assaying Consumer Reaction

The industrial-research group should make every effort to utilize new techniques in assaying consumer reaction. Some of the following methods can be used to obtain helpful information:

(1) Factory Panels: Selected groups in an organization were chosen as representatives of types of consumers and were given an opportunity to express a choice between new and old products. This method was used by Du Pont at an early stage of nylon stocking fabrication.

(2) Consumer-Expert Panels: "Reader-editors" of women's magazines have been used as testers. More frequently, they have been asked to give information through questionnaires on their preferences.

(3) Retail Group Buyers and Retail Salesmen Interviews: This source of information is usually influenced more by that which exists and is easily sold than by new and, as yet, less obvious wants.

(4) Retail Distributors, by Questionnaire or Interview

(5) Consumers, by Questionnaire or Interview: These techniques are used by market research groups employed by manufacturers to obtain evidence of potential wants indicated by choices between two or more possibilities. The 1948 Elmo Roper survey and report for the Carpet Institute, Inc., is an excellent example of a statistically planned study of consumer opinion, attitudes, and wants (see Appendix). This report led the American carpet industry into joint support, through its trade association, of a varied program of development of the style interests of consumers and of a periodic presentation of the new and novel in style features by its members. The report indicated that the major interest of the consumer was style, color, texture, and decorating attributes. It showed that the consumer was accepting as satisfactory, through experience over more than a century, the levels of quality and service attributes which existed. The conclusion that research and development, promotion, advertising, and selling should concentrate on the style and decorating aspects of soft floor coverings was obvious and was broadly accepted by the industry; the results in sales have been highly satisfactory.

(6) Limited-Area Sales of Product

(7) Sales-Promotion Personnel and Promotion Panels: A good deal of consumer reaction can be obtained by promoting the new in style to large groups. This technique has been developed to include electrical recording and totalizing of audience reaction.

(8) Research Studies of Subjective Consumer Responses: A large mattress manufacturer has financed

extensive research into the sleep patterns of carefully selected individuals.

(9) Studies of Responses to Various Types of Appeal in Advertising Copy

Conclusions

Research and development should use these techniques as an experimental and developmental process. Industry should encourage research which will lead to improvement in techniques with the hope that they will lead to new areas of knowledge in the broad research process.

During this era of uncertainty of the real value of these methods, the managers of textile research should extend and develop the channels of information that are regular and constant elements in the research process.

The textile industry must: support basic research and graduate education in textile science; develop adequate applied research facilities; support scientific and engineering societies in test-method development; participate in consumer-retailer activities; keep open channels of information from salesmen and buyers, styling and designing trends, and claims and complaints; study constantly competitors' and their own products for evidence of small differences that contribute to their being wanted; study changes in relative costs of raw materials which may change consumer preferences when reflected in changing price of products.

In a recent article in *Modern Industry* entitled "Revolution in Textiles," the third largest industry in the U. S. was described as a lumbering giant being galvanized into action by a series of revolutions that are bringing forth new and better products, materials, and equipment. The carpet industry in the U. S. is an important factor in these revolutions in textiles. The character of products has completely changed. In past years, product differences were characterized by mechanical weaving equipment names, such as velvet, Wilton, Axminster, chenille. New processes based on research on fiber properties have been developed which can transform weave structure into a myriad of textures which are no longer definable by structure. During this revolution, Alexander Smith's research program has been directed at improvements in the use of fibers and yarns which contribute uniquely either to economy of manufacture, to color, style, and appearance wants, or to service values. This emphasis on color, style, and texture developments was supported by a scientifically controlled survey of consumer preferences conducted by Elmo Roper for the Carpet Institute in 1948. Development of methods of improving the straighter wool fibers by crimping and development of the Harris invention of protection of wool fibers during color removal have had a broad response in many other sectors of the textile industry. We are convinced that product and process research controlled by the forces generated by all the elements of the research mechanism and process outlined in the present paper will ensure a successful program. We do not anticipate that new techniques of assaying consumer reaction will make as great a contribution to new product and process development as will our continued effort to keep the spiral of research moving upward by broadening all the channels of information and developing better liaison between all contributors to the research process, from the basic scientist to the ultimate consumer.

The process of research will, we believe, present to the consumer new items for selection. It will renew itself again and again by the discovery of small differences in the attributes of materials, processes, and product. These discoveries will make a constant, valuable, and inspiring contribution to the welfare and pleasure of the consumer.

Appendix

"A Report on Habits and Attitudes Concerning Rugs and Carpets" *

1. The purpose and use of the survey is quoted, in full, as an illustration of clear intention to obtain evidence of consumer attitudes:

"The purpose of the survey was to explore, as thoroughly as possible, the American consumer's attitude toward soft floor coverings—what importance people attach to them, their preferences, and how they regard the product. Most of the questions were designed to reveal consumer buying habits. While the information was obtained primarily for manufacturers, it is believed that it will be of equal value to retailers of carpets and rugs in selling and promotional activities. Much of the data provides facts which can be used by the retailer in day-to-day selling problems."

* An abstract from a consumer-reaction study prepared for Carpet Institute, Inc., by Elmo Roper, Apr., 1948.

2. Every effort was made by Mr. Roper to provide a scientifically designed "sample" of interviews which would give results typical of the entire population. The report summarizes the results of 6,122 interviews. The sample includes people only in top, upper-middle, and lower-middle economic levels. By choice, women in the sample outnumbered men by 5 to 1. The people interviewed were distributed proportionally throughout the country according to geographic location, age, economic level, marital status, type of dwelling, and position in family.

3. The questionnaires used were scientifically developed to exclude leading or slanted questions. They contained about 30 questions. The responses were analyzed in many ways. The tabulations required 277 pages.

4. Some interesting conclusions were:

Soft floor coverings lead as the article of furnishing considered most basic in a room.

When presented with a list of articles of furnishings, 50% said they would select the rug or carpet first.

People value rugs and carpets because of their contribution to the appearance of a room, by giving it color and tying it together.

People value rugs and carpets because they feel it makes rooms cozier, homier, and warmer.

Very few valued rugs and carpets chiefly because of softening sound or making housework easier.

There was a lively consumer interest in wall-to-wall carpets, mainly because they think them more attractive.

The right color in a rug or carpet is a major consideration.

Color was mentioned more than any other attribute as the problem in buying rugs and carpets.

Reasons for selecting present carpet or rug:

Color	56%
Pattern	20%
Inexpensive, good value	11%
Quality	10%
Texture or weave	7%
Does not show dirt or footprints	6%
Durability	5%

Women buy carpets and rugs for specific rooms.

Most people prefer to buy a rug or carpet that would last about 10 years than a more expensive one to last a lifetime; the reason is recognition of desire for changes in color scheme.

Textured types of rugs and carpets were preferred over conventional types.

Selected Publications in Fields Discussed

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Smith, H. DeW., Textile Fibers—An Engineering Approach to Their Properties and Utilization (Edgar Marburg Lecture), *Proc. Am. Soc. Testing Materials* **44**, 543 (1944).

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(Manuscript received Apr. 20, 1951.)

XIIth International Congress of Pure and Applied Chemistry

New York, September 10–13, 1951

Section 4: Elastomers and Plastomers

September 11, Tuesday Afternoon

Blue Room, Hotel McAlpin

P. H. Hermans, *Honorary Chairman*

J. H. Dillon, *Presiding*

2:00 P.M.—"Chemical Machining of Photosensitive Glass," by S. D. Stookey, Corning Glass Works

2:20 P.M.—"On Composition of Non-alkali and High Manganous Oxide Glass," by Bumpei Yoshiki, Asahi Glass Company

2:40 P.M.—"The Dyeing Behavior of Some Acid Dyes on Wool in Relation to their Physical Chemical Properties," by A. S. Fern, M. Fern, and T. Vickerstaff, Imperial Chemical Industries

3:00 P.M.—"L'Oxydation de la Cellulose en Milieu Cuprièthyléne Diamine" (to be presented in English), by J. Cyrot, Institut Textile de France

3:20 P.M.—"The Effect of Lithium Bromide Solutions on the Structure of Keratin Fibers," by Elsa Hambraeus and Richard Steele, Textile Research Institute

3:40 P.M.—"Correlation Between Sensitivity to Acid Hydrolysis and Skin Core Differentiation in Viscose Rayons," by P. H. Hermans, Inst. Voor Celluloseonderzoek

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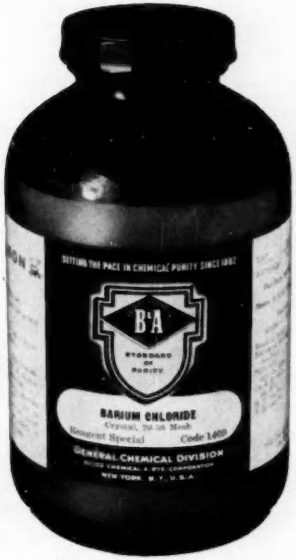

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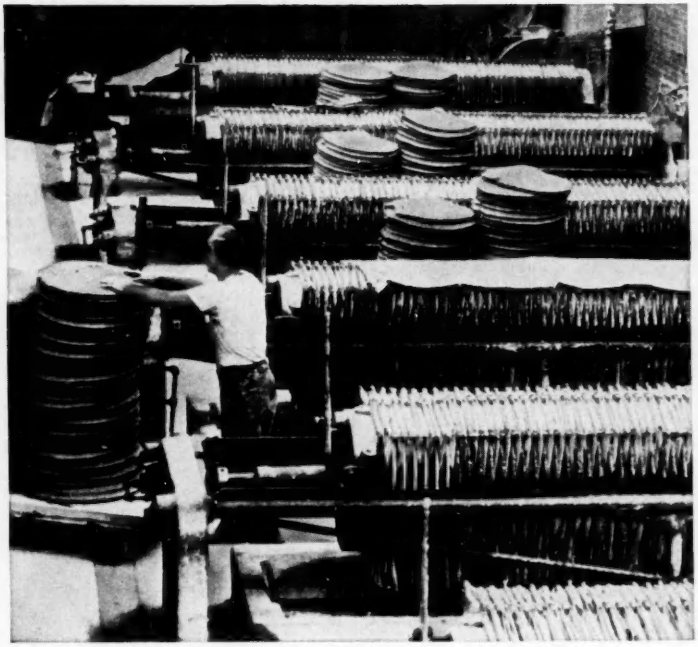
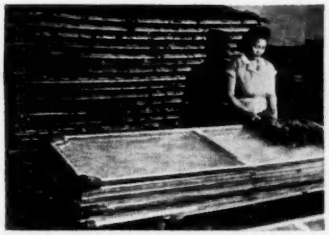


HIGH PRESSURES place heavy stress on filter sacks used in the ceramic industry. Filled with liquid clay, the sacks are squeezed in these accordion-like presses until water filters through the fabric and drains off, producing the clay cakes you see here.

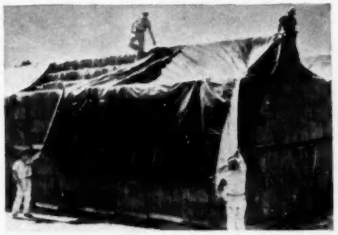
Filter sacks of tough Du Pont nylon fibers resist rupturing. They last up to ten times as long as ordinary sacks because of nylon's high resiliency, wet strength and imperviousness to mildew. Nylon sacks also speed production. For nylon fibers won't swell when wet . . . let water pass through more readily and with greater filtering efficiency.

This ability to stand up under the roughest treatment makes nylon useful in many industries. Pictures above show other examples of nylon's performance under conditions of severe wear.

Constant hammering of electric-typewriter keys wears ribbons tissue-thin, causes fuzzy, hard-to-read impressions. Thinner yet more durable nylon ribbons will outlast all other kinds . . . and they will produce sharp, clean impressions month after month.



Heat and humidity are chief causes of sagging, weakened nets in tobacco conditioning rooms. Nylon netting holds taut through high temperatures and extreme humidity. It won't deteriorate from mold or mildew; gives strong support far longer than previous materials.



Rot and weathering cut life span of tarpaulins used to protect hay stored outdoors at stockyards. Nylon "tarps" stand up well in adverse weather . . . promise to last three to five times longer. They're also easier to handle—weigh only half as much as ordinary tarpaulins.

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